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Titanacyclobutanes From Radical Alkylation of Substituted π-Allyl Titanocene(III) Complexes and Conversion to 4- and 5-Membered Organic Ring Systems

by

Charles Ashton Garett Carter ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Department of Chemistry

Edmonton, Alberta

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The undersigned certify that they have read, and recommended to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled: **Titanacyclobutanes From Radical Alkylation of Substituted π-Allyl Titanocene(III) Complexes and Conversion to 4- and 5-Membered Organic Ring Systems**; submitted by Charles Ashton Garett Carter in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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To my parents and my wife, Ana.

Abstract

The first part of this work focuses on the development of new titanocene templates that can effectively mediate regioselective central carbon alkylation of substituted π-allyl complexes. The *ansa*-[1]-bridged titanocene(III) template, which has more room in the wedge between the cyclopentadienyl rings, promotes free radical alkylation reaction to η^3-crotyl and η^3-cinnamyl complexes, providing 2,3-disubstituted titanacyclobutane complexes in good to excellent yields. Interestingly, only complexes with the *meso-ansa*-[1]-bridged bis(1,1'-disubstituted-cyclopentadienyl)titanium template demonstrate this reactivity; the corresponding *rac* analogues do not. This investigation also shows that radical addition to these η^3-allyl complexes is significantly facilitated by electron-donor ancillary ligands. The trimethylsilyl- and isopropyl-substituted *ansa*-bridged titanocene templates support central carbon alkylation, but unsubstituted *ansa*-bridged templates fail to give this reactivity. More significantly, the unbridged aminotitanocene η^3-crotyl and η^3-cinnamyl complexes with strong electron-donor dialkylamino substituents, are good substrates for regioselective radical addition reactions. These results provide strong support for the hypothesis that enhanced electron density at the metal center, provided inductively or mesomerically, can promote radical alkylation of substituted π-allyl complexes. Addition of nucleophiles to cationic permethyltitanocene(IV) π-allyl complexes reveals that this template only supports regioselective alkylation to the η^3-allyl moiety.

The second part of this work is an investigation into small molecule functionalization of titanacyclobutane complexes, providing access to both four- and five-membered carbocyclic ketones. Controlled single insertion of carbon monoxide and alkyl isonitriles into the titanacyclobutane ring efficiently gives cyclobutanones and cyclobutanimines. This novel reactivity is general for β-substituted titanacyclobutane complexes, but is dependent on the nature of the ancillary ligands and the α-substituent in 2,3-disubstituted titanacycles.

This investigation also demonstrates that double insertion reactions of titanacyclobutane complexes readily give functionalized cyclopentanones and cyclopentenones subsequent to demetallation. An unprecedented oxidative cleavage of titanium cyclopentenediolates using triphosgene is also demonstrated. The high efficiency of this process makes it an attractive and potentially general demetallation strategy for other enediolate complexes. These carbon-carbon bond forming reactions clearly demonstrate the tremendous potential of these titanium-mediated processes as a useful synthetic tool for the synthesis of structurally diverse carbocyclic compounds.

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List of Abbreviations

Å	Angstrom
AIBN	2,2'-Azobisisobutyronitrile
atm	Atmosphere
Bu	Butyl
calcd	Calculated
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
Cy	Cyclohexyl
COSY	correlated spectroscopy
EHMO	Extended Hückel Molecular Orbital
Et	Ethyl
equiv	Equivalent
FMO	Frontier Molecular Orbital
g	grams
GC	Gas Chromatography
h	hour(s)
Hz	Hertz
HOMO	Highest Occupied Molecular Orbital
i	iso
IR	Infrared
L	liter
LUMO	Lowest Unoccupied Molecular Orbital
M	Metal
Me	Methyl
mL	milliliter

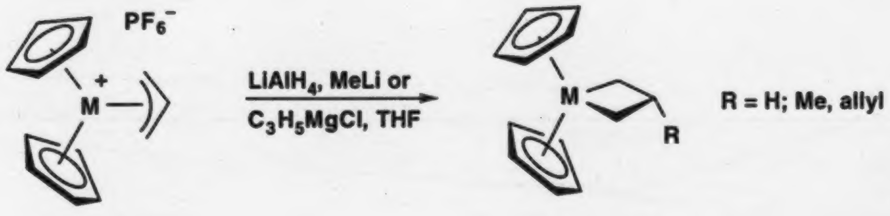
MS	Mass Spectrometry
n	normal
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
OTf^-	Trifluoromethanesulfonate
Ph	Phenyl
pm	picometer
ppm	parts per million
Pr	Propyl
psig	Pounds per square inch gauge pressure
R	Alkyl Group
SOMO	Singly Occupied Molecular Orbital
t	tertiary
THF	Tetrahydrofuran
TMEDA	N,N,N',N'-Tetramethylethylenediamine
TMS	Trimethylsilyl
X	Halide
η	hapticity
μL	microliter

1. INTRODUCTION AND HISTORICAL PERSPECTIVE OF CENTRAL CARBON ALKYLATION REACTIONS OF η^3-ALLYL COMPLEXES

1.1. Nucleophilic Addition to Cationic η^3-Allyl Complexes

Central carbon alkylation of transition metal η^3-allyl complexes was first reported in 1976 by M.L.H. Green in an investigation of nucleophilic addition to the group VI metallocene π-allyl complexes.[1,2] In this study, cationic π-allyl complexes **1** and **2** were treated with various nucleophiles in THF and gave the corresponding β-substituted metallacyclobutane complexes **3** and **4** (Scheme 1.1). This was an unexpected reactivity pattern for transition metal π-allyl complexes, which were known at that time to undergo nucleophilic attack only at the terminal allyl carbon to form alkene complexes.[3-8] In the absence of mechanistic studies, it was proposed that the metallacyclobutane products were formed from direct attack at the central carbon of the allyl ligand and not from initial attack at the metal followed by rearrangement (Scheme 1.1).

Scheme 1.1



	M			M
1	W		3	W
2	Mo		4	Mo

A charge-control argument, rationalized in the Davies-Green-Mingos (DGM) rules by a perturbational molecular orbital approach that examines the effect of complexation on the charge distribution in the HOMO of the allyl moiety, was proposed to explain this regioselectivity.[9] For electron-rich metal fragments, such as was ascribed to the d^2 Cp_2M

systems (M = Mo, W), the terminal carbon atoms are assumed to be partially negative relative to the central carbon atom as a result of d→π* back-donation into the Ψ_2-allyl molecular orbital (Figure 1.1). A consequence of this is that the nucleophile is directed to the relatively more electrophilic central carbon of the allyl ligand to give the observed products.

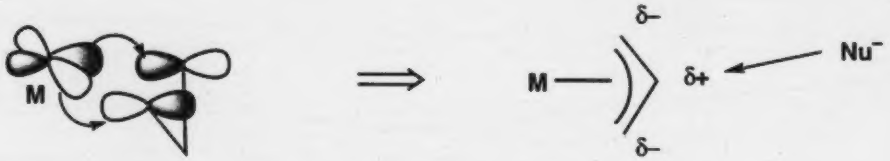
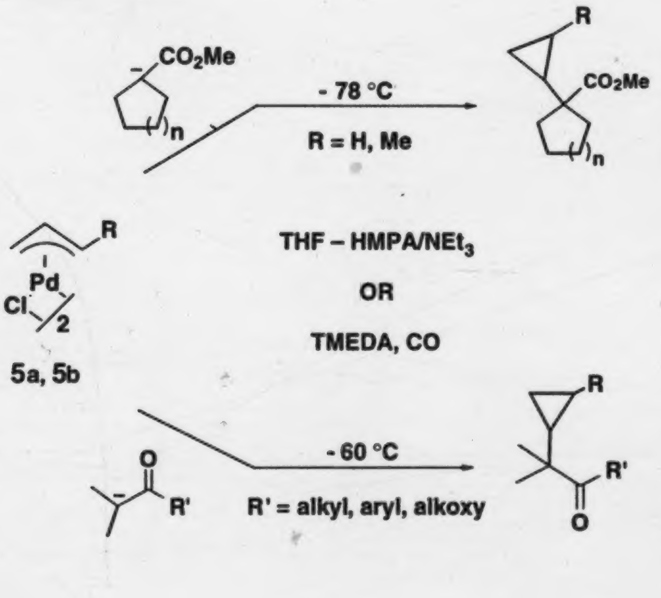


Figure 1.1. Charge Control Argument for Regioselectivity of Nucleophilic Addition

Since this first report, there have been several observations of this reactivity pattern with other transition metal π-allyl complexes. For instance, in certain cases, palladium

Scheme 1.2


CO₂Me
n
- 78 °C
R = H, Me
R
CO₂Me
n
R
Pd
Cl
2
THF – HMPA/NEt₃
OR
TMEDA, CO
O
R'
- 60 °C
R' = alkyl, aryl, alkoxy
R
R'
O

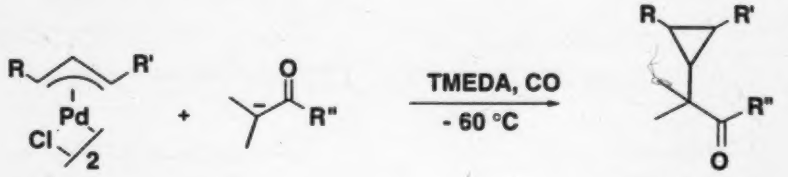
5a, 5b

	n	R	Yield(%)
6a	1	H	72
6b		H	83
7a	2	CH_3	84
7b		CH_3	78

	R	R'
8 a	H	alkyl (65%)
8 b	H	aryl (54-63%)
8 c	H	alkoxy (13%)
9	Me	alkoxy (70%)

and platinum π-allyl complexes give substituted cyclopropanes from central carbon alkylation by certain nucleophiles, followed by reductive elimination.[10-16] Typically however, η^3-allyl palladium and platinum complexes undergo terminal addition for weak nucleophiles and metal addition for strong nucleophiles, such as the ones discussed here.[3,8] Various enolates and carbon nucleophiles have been successfully used in this reaction, as illustrated in Scheme 1.2. The conditions necessary for this regioselectivity to be obtained are highly specific, requiring either HMPA/Et_3N or TMEDA/CO in THF at -60 °C.[13,15] The nature of the substituents on the allyl ligand affects the outcome of the reaction, in that 1,3-dimethylallyl complexes (such as **10a** and **10b**, Scheme 1.3) fail to give cyclopropanes, but replacing one of the methyl groups with a phenyl group reinstates central carbon selectivity to give trisubstituted cyclopropanes **11a** and **11b**.[11] This apparent facilitation of the cyclopropanation reaction by the phenyl substituent is

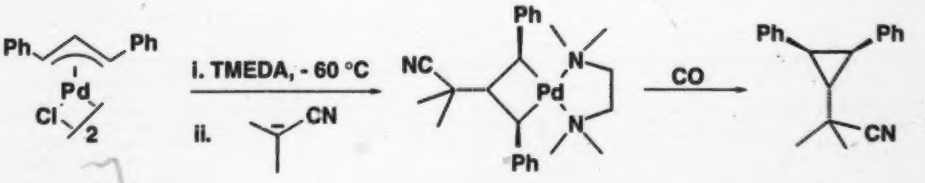
Scheme 1.3



10a R, R' = Me
10b R = Me, R' = Ph

11a R, R' = Me (0 %)
11b R = Me; R' = Ph (82 %)

Scheme 1.4



12

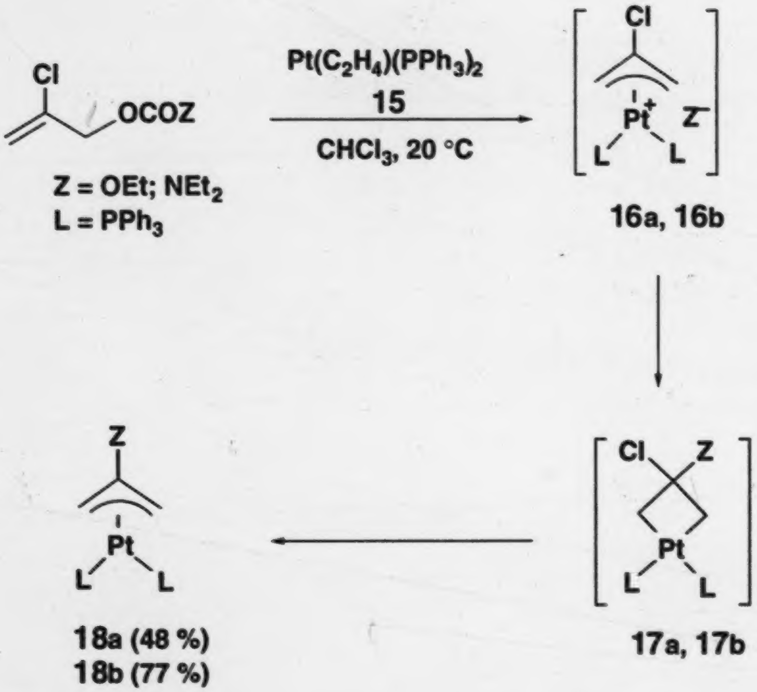
13 (55 %)

14

referred to as an 'aryl effect', but the reasons for this observation are not understood. Isolation of the palladacyclobutane **13** and its subsequent transformation to cyclopropane **14** confirms the intermediacy of a metallacyclobutane species in these cyclopropanation reactions (Scheme 1.4).[10]

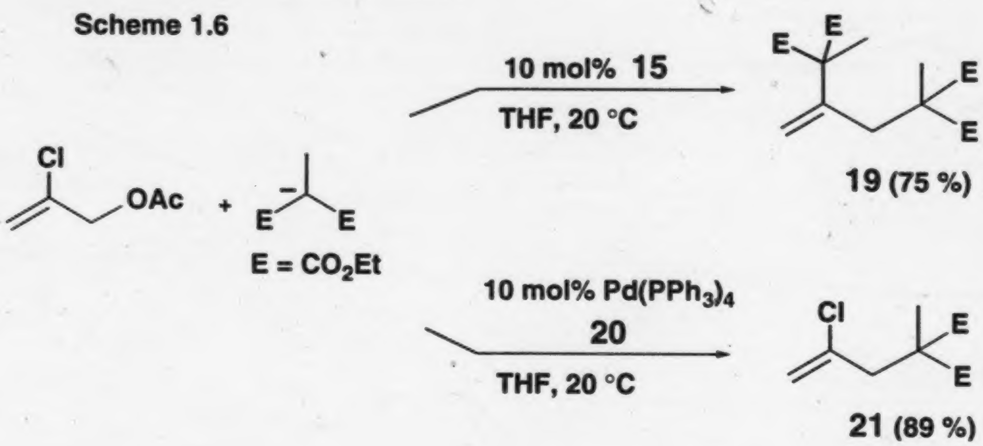
Some isoelectronic platinum π-allyl complexes also show similar reactivity towards nucleophiles[14,16] and recently Murai reported that nucleophilic substitution at the central carbon of β–substituted platinum π-allyl complexes (Scheme 1.5).[17] As shown in Scheme 1.5, the *in situ* generated 2-chloro-allylplatinum complexes **16a** and **16b** undergo nucleophilic addition to give a transient β,β-disubstituted platinacyclobutanes **17a** and **17b**, which subsequently lose chloride ion to give the new 2-substituted π-allyl

Scheme 1.5


Cl
OCOZ
Z = OEt; NEt₂
L = PPh₃
Pt(C₂H₄)(PPh₃)₂
15
CHCl₃, 20 °C
Cl
Pt+
Z⁻
L
L
16a, 16b
Cl
Z
Pt
L
L
17a, 17b
Z
Pt
L
L
18a (48 %)
18b (77 %)

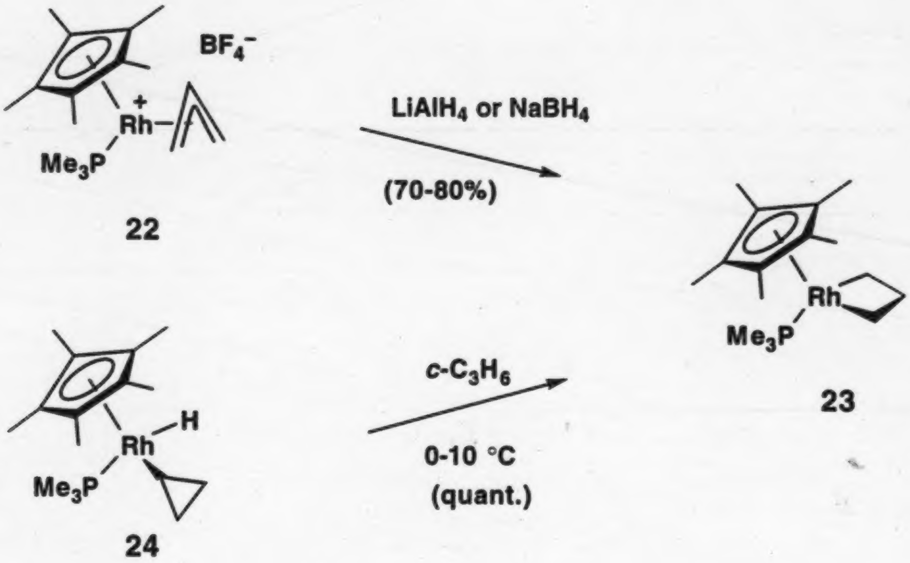
complexes **18a** and **18b**. A catalytic version of this reaction was also reported, which is envisioned to enhance the synthetic utility of this methodology (Scheme 1.6). This reaction is sensitive to the nature of the catalyst, since use of $Pd(PPh_3)_4$ **20** as catalyst gave the vinyl chloride **21** exclusively (Scheme 1.6).[17-19]

Scheme 1.6



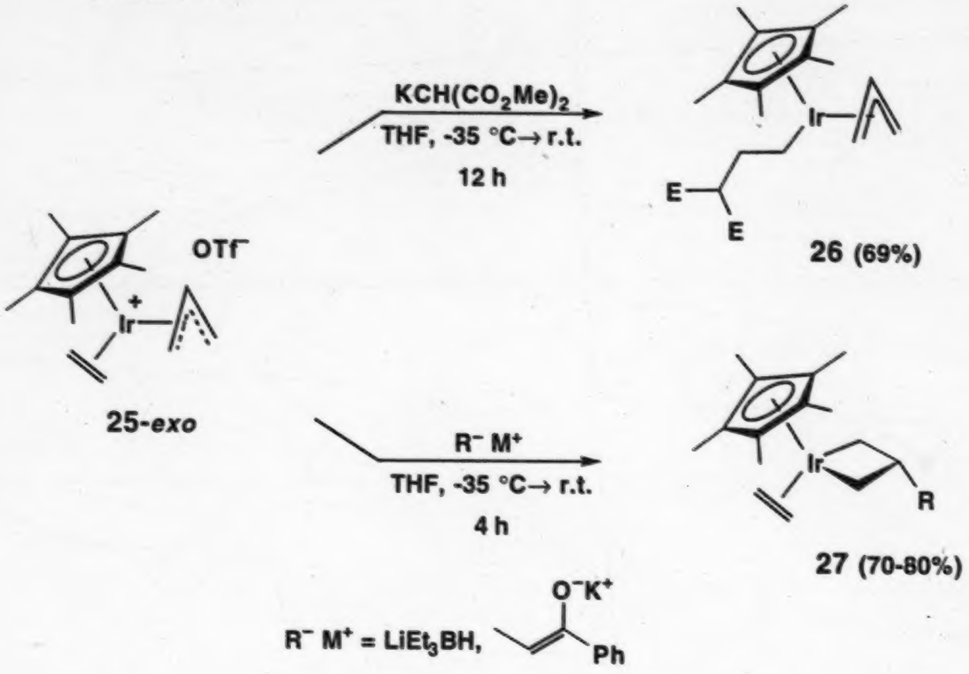
The half-sandwich Group IX metallocene π-allyl complexes $[Cp^*(L)M(\eta^3\text{-allyl})]^+X^-$ (M = Rh, Ir; X = BF_4, PF_6, Cp* = C_5Me_5) also demonstrate this reactivity. Bergman first reported that $[Cp^*(PMe_3)M(\eta^3\text{-allyl})]^+BF_4^-$ (M = Rh, Ir) complexes undergo nucleophilic addition to the central carbon of the allyl ligand when treated with hydride reagents (Scheme 1.7).[20-23] For instance, the rhodacyclobutane complex **23** is formed from addition of hydride to the central carbon position of the cationic π-allyl rhodium complex **22**. The former complex is also formed from an intramolecular thermal rearrangement of the hydrido cyclopropyl complex **24** at low temperature. Deuterium labeling studies of this system and additions to an analogous iridium system[20,22] show that the nucleophilic addition reaction indeed proceeds by direct hydride addition to the central carbon of a π-allyl metal complex, and not by initial metal addition followed by rearrangement.[20-22]

Scheme 1.7



A more detailed investigation into the reactivity of this system was reported by the Stryker group, resulting in some very important findings.[24-31] The regioselectivity of the nucleophilic addition was found to be dependent on the nature of the nucleophile as well as on the configuration of the allyl ligand (Scheme 1.8).[28] The *exo* cationic iridium allyl ethylene complex **25-*exo***, when treated with the potassium enolate of dimethylmalonate yields exclusive addition to the ethylene carbon, as predicted by the DGM rules for kinetically controlled addition reactions. In contrast, however, the potassium enolate of propiophenone undergoes exclusive central carbon alkylation to give iridacyclobutane complex **27**. This regioselectivity is in direct contradiction of the DGM rule that predicts kinetic nucleophilic addition will occur preferentially to an even (2-carbon), open polyene over addition to an odd (3-carbon), open polyene.[9] Further, the *endo* isomer, **25-*endo***, undergoes alkylation with dimethylmalonate anion exclusively at the *terminal* carbon of the allyl ligand to give the bisolefin complex **28** as a mixture of stereoisomers, but gives

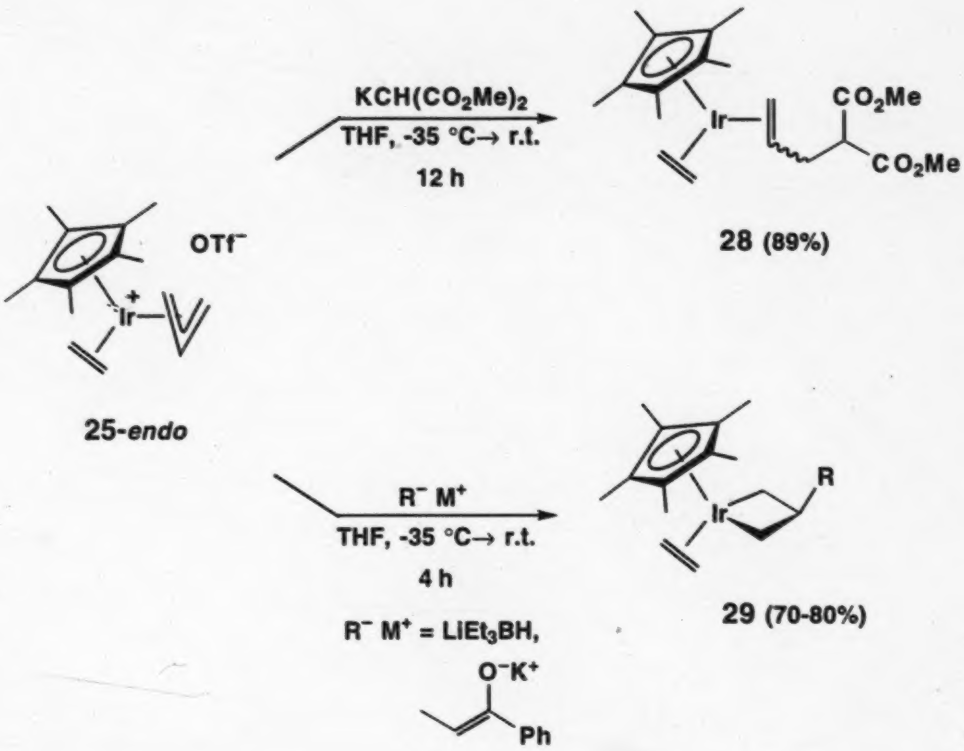
Scheme 1.8



central carbon alkylation with hydride and the potassium enolate of acetophenone to give complex **29** (Scheme 1.9).[28] The regioselectivity of these reactions are also in contradiction of the DGM rules. Additionally, using related rhodium complexes it was shown that the *endo, anti* crotyl complex **30** gives the *Z*-olefin complex **31** from terminal carbon addition, whereas the thermodynamically more stable *exo, syn* isomer **30** gives the central carbon alkylation product **32** predominantly in most cases (Scheme 1.10). These findings suggest that the coordination geometry of the complex may be more important than the degree of electron-richness in determining the regiochemistry of kinetic nucleophilic addition to transition metal π-allyl complexes. Taken together, these results call for an alternative rationalization for the selectivity for central carbon alkylation.

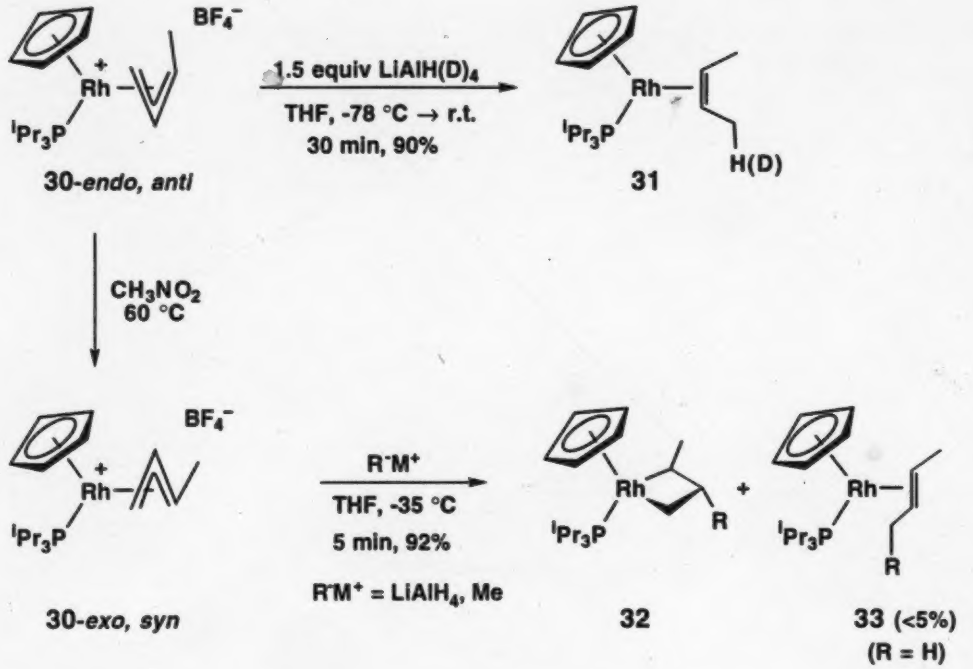
Another significant finding from these studies is that the kinetic addition of even stabilized nucleophiles can occur preferentially at the central carbon position (Scheme

Scheme 1.9


KCH(CO₂Me)₂
THF, -35 °C→ r.t.
12 h
CO₂Me
CO₂Me
Ir
28 (89%)
OTf⁻
Ir
25-endo
R⁻ M⁺
THF, -35 °C→ r.t.
4 h
R⁻ M⁺ = LiEt₃BH,
O⁻K⁺
Ph
R
Ir
29 (70-80%)

1.11), but be followed by re-ionization and re-addition to give the thermodynamically preferred terminal carbon adduct **36**, a process that can be catalyzed by the presence of Lewis acids (Equation 1.1).[24-27,30,32,33] A low temperature trapping experiment of the alkylation reaction mixture gives the cyclopropane derivative **37** as the major product, confirming that the rhodacyclobutane complex **35** is the kinetic product (Scheme 1.11). Experimental evidence in support of a re-ionization mechanism for metallacyclobutane rearrangement is obtained from thermolysis of the iridacyclobutane complex **41** in the presence of excess dimethyl malonate to give the olefin adduct **42** (Scheme 1.12).[30,34] These results confirm the kinetic preference for nucleophilic addition to the central carbon of the η^3-allyl ligand in this system and demonstrate that despite the highly

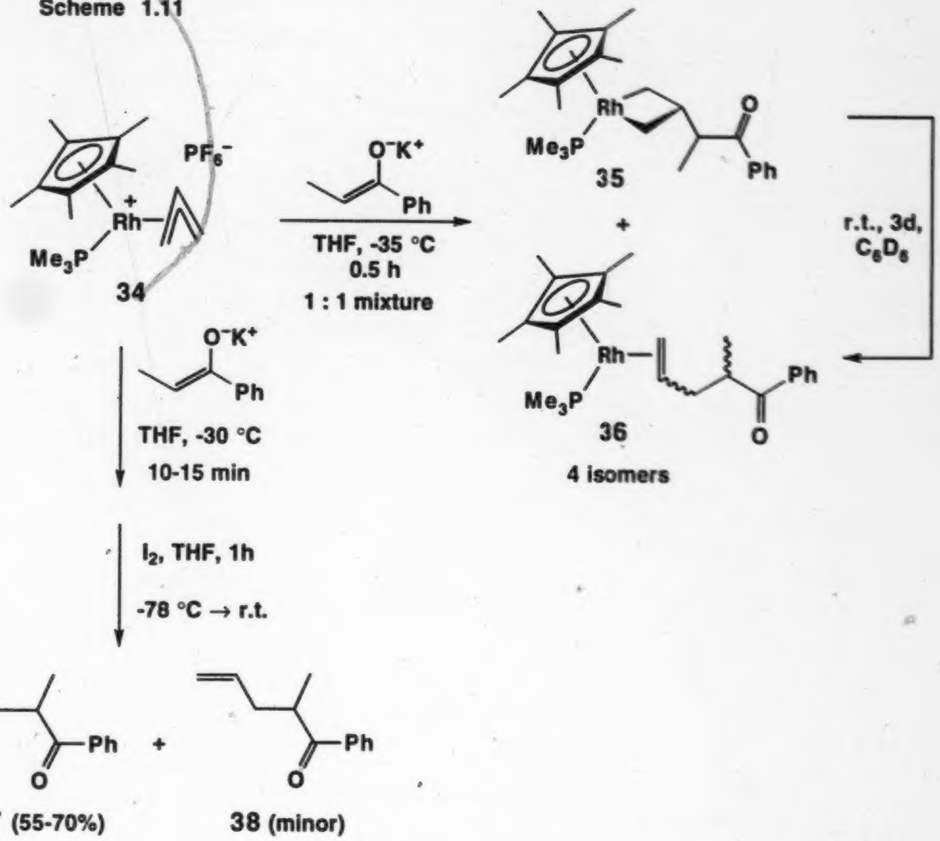
Scheme 1.10


BF$_4^-$
+
Rh
^{i}Pr$_3$P
30-*endo, anti*
1.5 equiv LiAlH(D)$_4$
THF, -78 °C → r.t.
30 min, 90%
Rh
^{i}Pr$_3$P
H(D)
31
CH$_3$NO$_2$
60 °C
BF$_4^-$
+
Rh
^{i}Pr$_3$P
30-*exo, syn*
R$^-$M$^+$
THF, -35 °C
5 min, 92%
R$^-$M$^+$ = LiAlH$_4$, Me
Rh
^{i}Pr$_3$P
R
32
+
Rh
^{i}Pr$_3$P
R
33 (<5%)
(R = H)

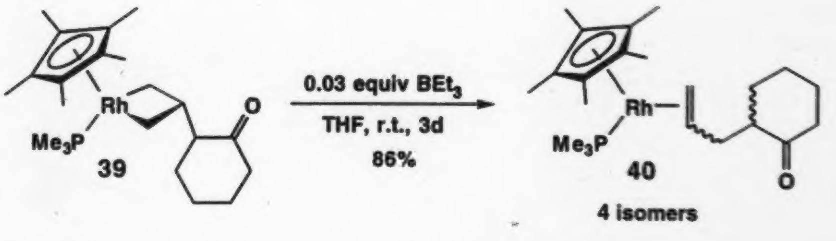
electron rich metal center, the lower valent olefin complexes are thermodynamically more stable than the nominally higher oxidation state metallacyclobutane complexes, contradicting an earlier claim.[1]

To get a clearer picture of the factors that are responsible for determining the regioselectivity of nucleophilic addition to these π-allyl complexes, various molecular orbital calculations have been reported.[18,35,36] These investigations focused on the symmetry characteristics and the relative potential energies of the frontier molecular orbitals that may be involved in controlling the regioselectivity of these reactions.[35,37] According to this model, for most late metal π-allyl complexes, one of two vacant low-lying molecular orbitals of different symmetry could act as the LUMO for the complex and hence determine the regiochemical outcome of these reactions. Nucleophilic addition

Scheme 1.11

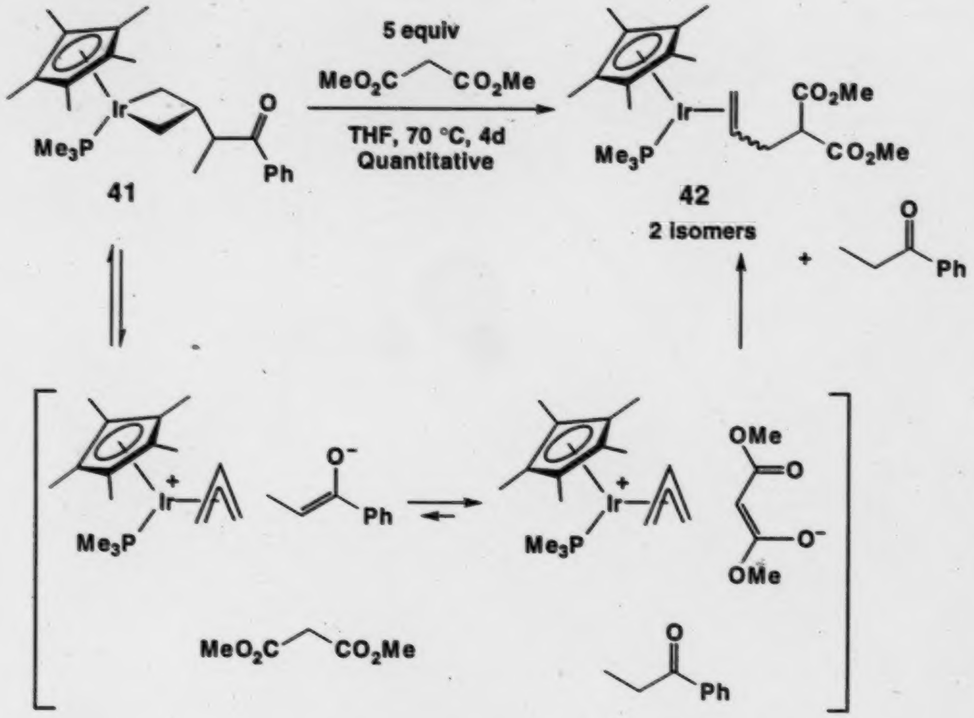

PF6−
Rh
Me3P
34
O−K+
Ph
THF, -35 °C
0.5 h
1 : 1 mixture
Rh
O
Me3P
35
Ph
+
Rh
Me3P
36
Ph
O
4 isomers
r.t., 3d,
C6D6
O−K+
Ph
THF, -30 °C
10-15 min
I2, THF, 1h
-78 °C → r.t.
Ph
O
+
Ph
O
37 (55-70%)
38 (minor)

would occur at either of the terminal carbon positions of the allyl ligand if the LUMO of the π-allyl complex is a combination between a metal-based orbital and the *non-bonding orbital* (Ψ_2) of the allyl ligand, since only the terminal carbon atoms have orbital coefficients associated with them. On the other hand, if the LUMO is a combination between a metal-based orbital and the *π*-orbital* (Ψ_3) of the allyl ligand, central carbon


Rh
O
Me3P
39
0.03 equiv BEt3
THF, r.t., 3d
86%
Rh
Me3P
40
O
4 isomers

(1.1)

Scheme 1.12



alkylation would be observed since the central carbon atom has a larger orbital coefficient than the terminal carbon atoms.[35] This prediction finds support in the reactions of the π-allyl complexes of the Group VI (W, Mo)[1,2] and IX (Co, Rh, Ir),[20-23,26-28,30,32-34] however, it fails to predict the observed reactivity of the platinum and palladium π-allyl complexes[10-15,17,36,38] discussed earlier.

A more empirical analysis, reported initially by Musco[36] and Hofmann[10-13] and then recently re-investigated by Bäckvall,[18] for platinum and palladium π-allyl complexes rationalized that the nature of the ancillary ligands plays an important role in determining the relative ordering of these two frontier molecular orbitals, hence influencing the regiochemical outcome of these reactions. This model predicts that strong σ-donating ligands (*e.g.* TMEDA) stabilize the symmetric molecular orbital, which is a combination between a metal-based d-orbital (a' orbital) and the π*-orbital of the allyl ligand relative to the antisymmetric orbital, making the former the LUMO.[18] This latter prediction is supported by experimental data (Scheme 1.5) which it was developed to explain.[13,15,18]

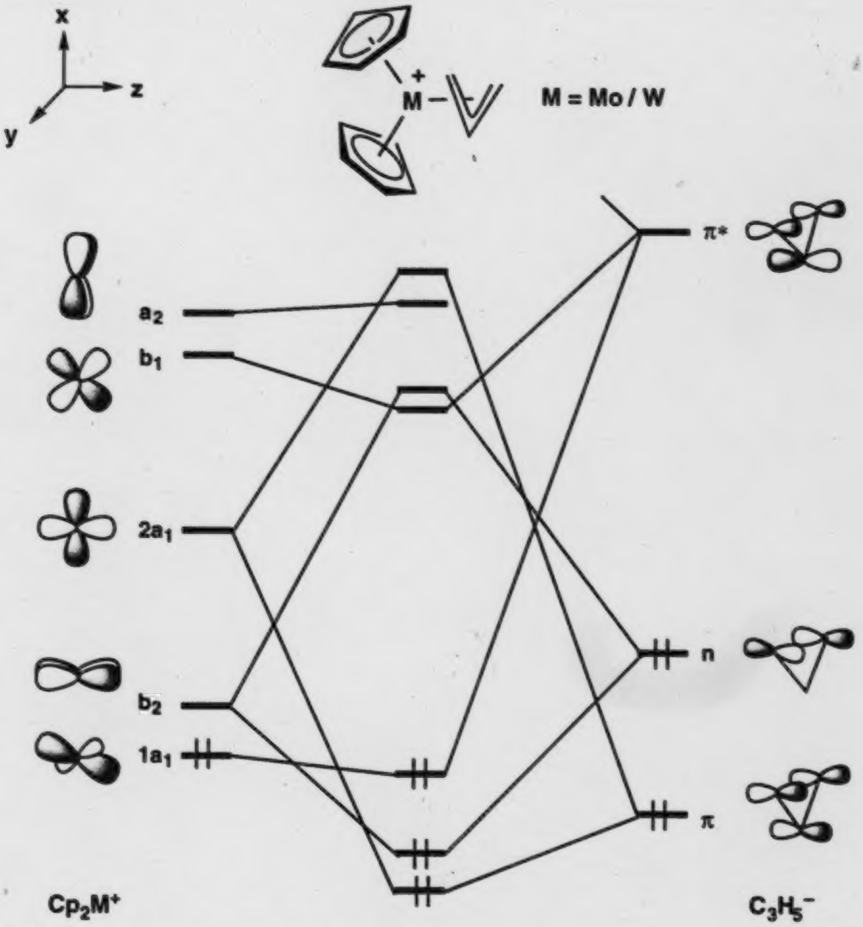


Figure 1.2. EHMO Energy Level Diagram for d^2 Group VI Metallocene π-Allyl Complex

In their report of MO calculations on a variety of π-allyl systems, Curtis and Eisenstein tentatively predict that cationic, pseudo-tetrahedral, d^0 Group IV π-allyl complexes also *might* undergo nucleophilic addition at the central carbon position.[35] Inspection of the MO energy level diagram for the d^2 Group VI (Figure 1.2) and d^0 Group IV (Figure 1.3) metallocene π-allyl complexes shows that the frontier molecular orbitals in both systems have similar symmetry characteristics. In the case of the Group VI complexes, the LUMO is the *bonding* combination of the b_2 orbital of the metal and

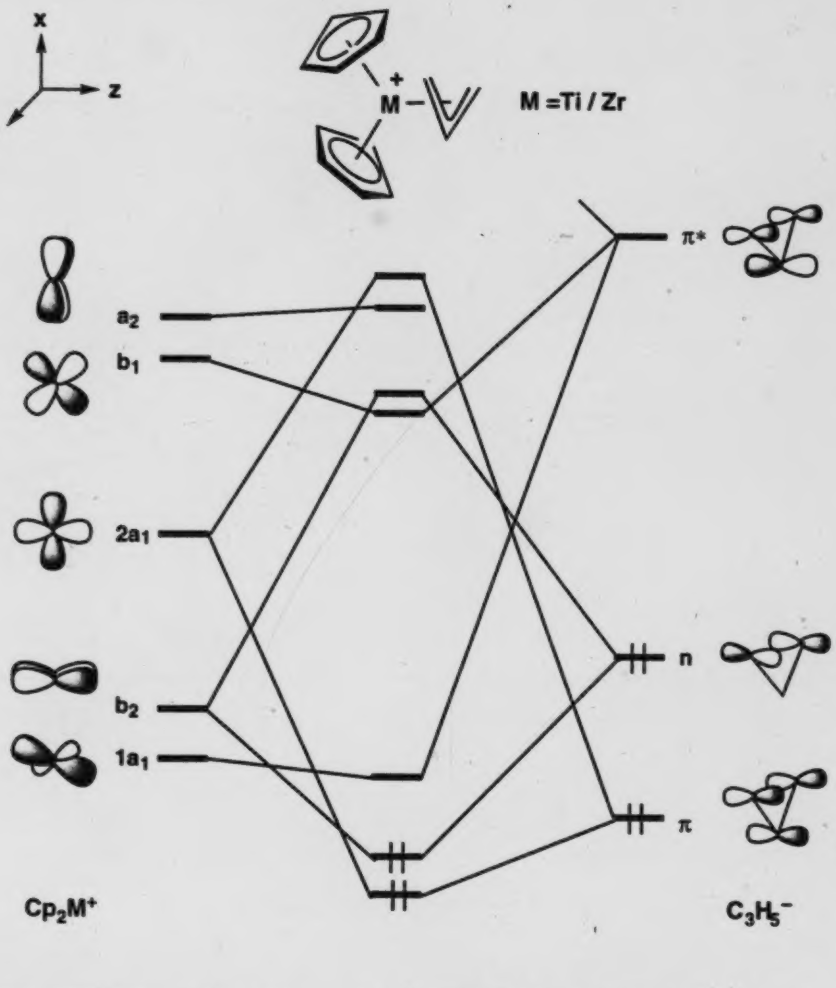


Figure 1.3. EHMO Energy Level Diagram for d^0 Group IV Metallocene π-Allyl Complex

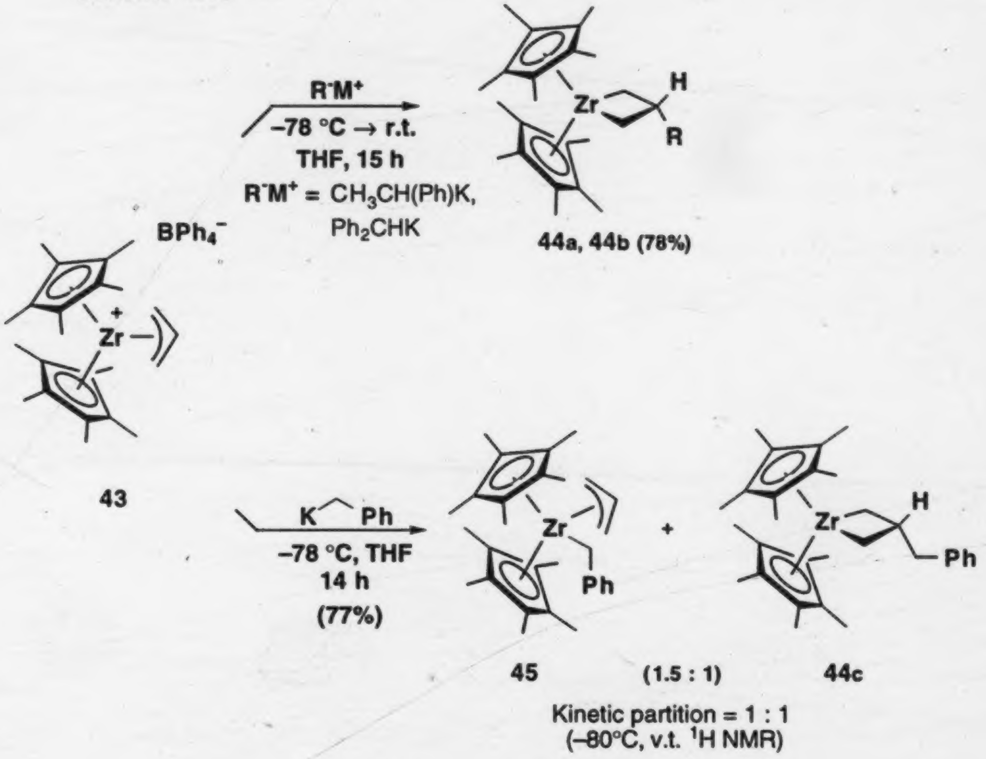
the π^*-orbital of the allyl ligand (Figure 1.2), whereas for the Group IV complexes, the LUMO is the *bonding* combination between the $1a_1$ orbital of the metal and the π^*-orbital of the allyl ligand (Figure 1.3). In the latter case, the LUMO is mostly $1a_1$. Consequently, successful central carbon alkylation of these d^0 Group IV π-allyl complexes would indeed be a true test of the frontier molecular orbital rationalization proposed to explain kinetic central carbon nucleophilic addition to π-allyl complexes, since these complexes completely lack d-electrons for $d \rightarrow \pi^*$ back-bonding.

The first experimental evidence for this reactivity pattern in d^0 Group IV π-allyl complexes was reported recently by the Stryker group.[25,34] Addition of sterically significant nucleophiles (diphenylmethylpotassium or 1-phenylethylpotassium) to the highly reactive zirconocene π-allyl complex, **43**, afford regioselective alkylation of the central carbon to give β-substituted zirconacyclobutane complexes **44a** and **44b** (Scheme 1.13).[25] Smaller nucleophiles (MeMgCl, MeLi or allylmagnesium chloride) attack exclusively at the relatively sterically accessible metal center. However, benzylpotassium, a nucleophile of intermediate steric profile, shows a kinetic partitioning, leading to mixtures of the allyl benzyl complex **45** and the β-benzylzirconacyclobutane complex **44c** as determined by low temperature NMR spectroscopic analysis of the reaction in progress (Scheme 1.13). It should be noted, however, that the allyl benzyl complex **45** rearranges quantitatively to zirconacyclobutane **44c** above room temperature, indicating that the zirconacyclobutane complex is the thermodynamically more stable of the two products. The observation of metal addition is not too surprising in this system, given that the LUMO in these 16-electron complexes is *mostly* $1a_1$ metal character.

Further support for the frontier molecular orbital rationalization of central carbon alkylation is garnered from the reactivity of the cationic d^0 titanium complex,

$[Cp^*{}_2Ti(\eta^3\text{-}C_3H_5)]^+BPh_4^-$ **46**,[25,34] which also demonstrates central carbon alkylation reaction using several nucleophiles having widely differing steric profiles and nucleophilicities (Scheme 1.14).[25,39] Titanocene complex **46** affords exclusively central

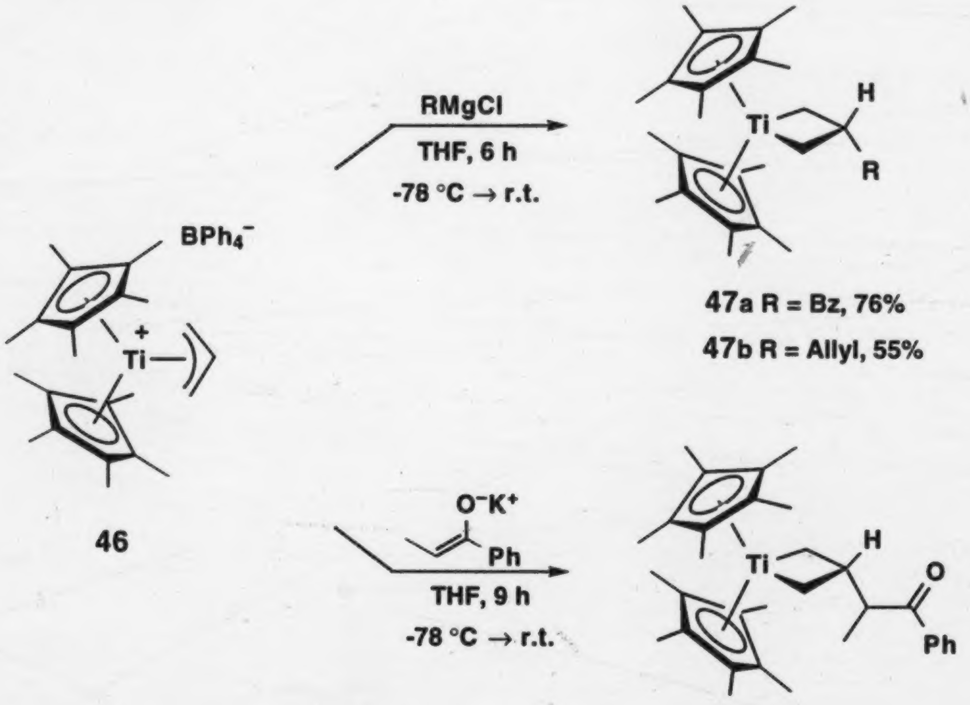
Scheme 1.13


R⁻M⁺
–78 °C → r.t.
THF, 15 h
R⁻M⁺ = CH₃CH(Ph)K, Ph₂CHK
BPh₄⁻
Zr
H
R
44a, 44b (78%)
43
K Ph
–78 °C, THF
14 h
(77%)
Ph
+
45
(1.5 : 1)
44c
Kinetic partition = 1 : 1
(–80°C, v.t. ¹H NMR)

carbon alkylation products instead of metal alkylation with allyl or benzyl Grignard reagents, presumably because the smaller ionic radius of titanium (0.64 pm) provides more steric shielding of the metal center than does zirconium (0.74 pm). Unlike the zirconium allyl complex **43**, this complex adds the potassium enolate of acetophenone regioselectively to the central position of the allyl moiety, giving titanacyclobutane **47c**, presumably because of the lower oxophilicity[40] of titanium versus zirconium.

Several spectroscopic features of these Group IV metallacyclobutane complexes are diagnostic: shielded α-proton resonances (between 1.0 to 2.0 ppm) and highly shielded β-proton resonances (upfield of 0.5 ppm), deshielded α-carbon resonances (between 60 and 65 ppm), and an only slightly shielded β-carbon resonance (between 20 and 30 ppm).[25,34,39,41,42] In addition, the methyl resonances on the two Cp* rings are chemically inequivalent as a consequence of the top-to-bottom dissymmetry of the metallacyclobutane complexes.

Scheme 1.14



46

47a R = Bz, 76%

47b R = Allyl, 55%

47c 88%

1.2. Radical Additions to Neutral η^3-Allyl Complexes

The FMO prediction that governs the regioselectivity of nucleophilic addition to the cationic group IV π-allyl complexes, $[Cp^*_2M(\eta^3\text{-allyl})]^+BPh_4^-$ (M = Zr, Ti) **43** and **46**[25,35,37] can be extended to predict free radical addition reactions to the corresponding neutral d^1 titanium(III) allyl complexes. As shown in Figure 1.4, the singly-occupied frontier molecular orbital (*i.e.*, the SOMO) of these complexes is the same bonding

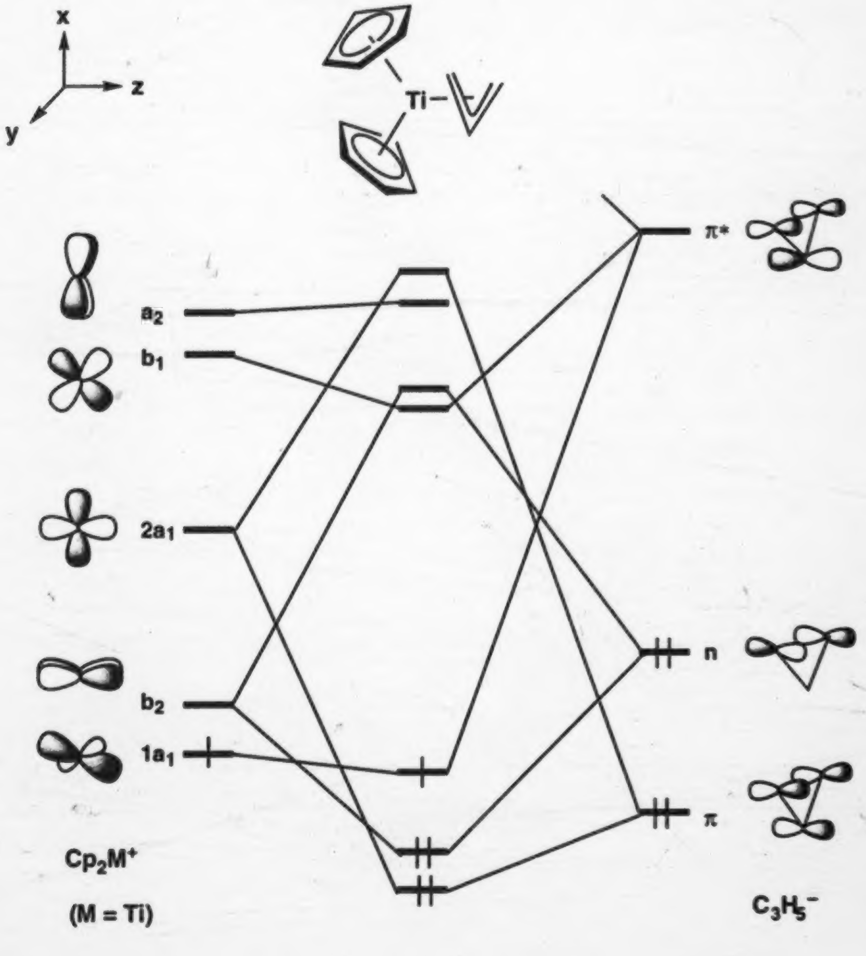
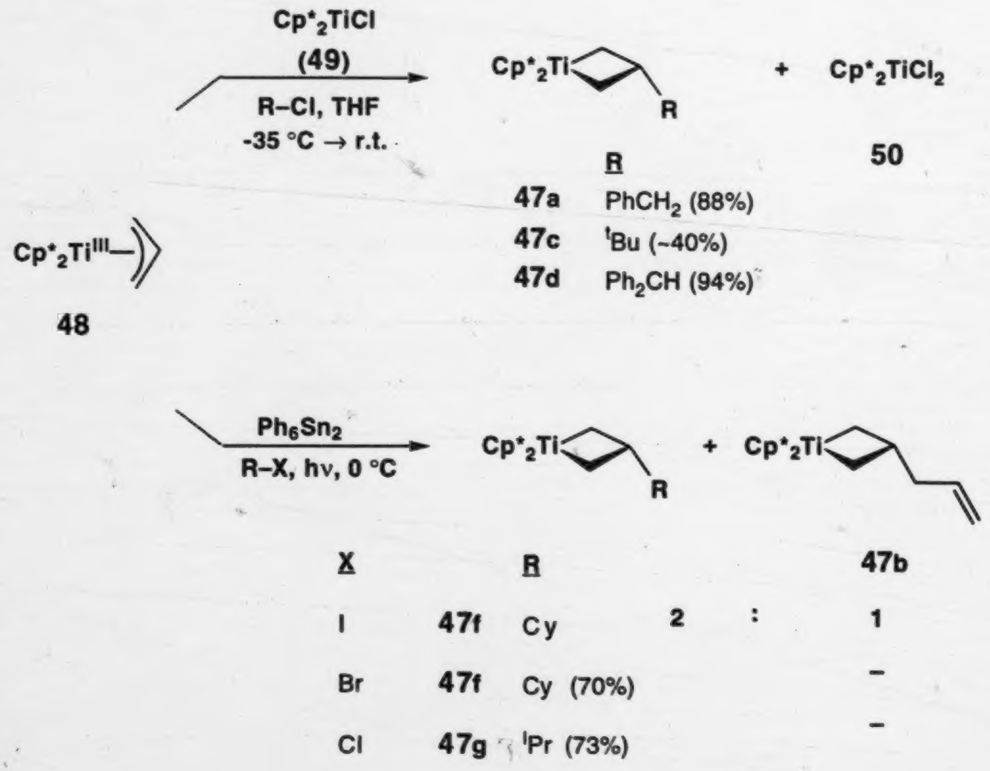


Figure 1.4. EHMO Energy Level Diagram for d^1 Group IV Metallocene π-Allyl Complex

combination of the metal $1a_1$ orbital and the π^* orbital of the allyl fragment as was the LUMO in the cationic series. It is expected, therefore, that these complexes should elicit central carbon alkylation in reactions with organic free radicals.

The first central carbon alkylation of neutral d^1 titanocene π-allyl complexes of titanium with organic free radicals has, in fact, been recently reported by Casty and Stryker.[39,42] This study reported that allyl complex, $Cp^*_2Ti(\eta^3\text{-}C_3H_5)$ **48**, when treated with Cp^*_2TiCl **49** and an alkyl halide, successfully undergoes central carbon alkylation to yield β-alkyl titanacyclobutane complexes **47a**, **47c** and **47d** (Scheme 1.15).[39,42] This radical generating strategy, however, is limited to benzylic and tertiary organic radicals

Scheme 1.15

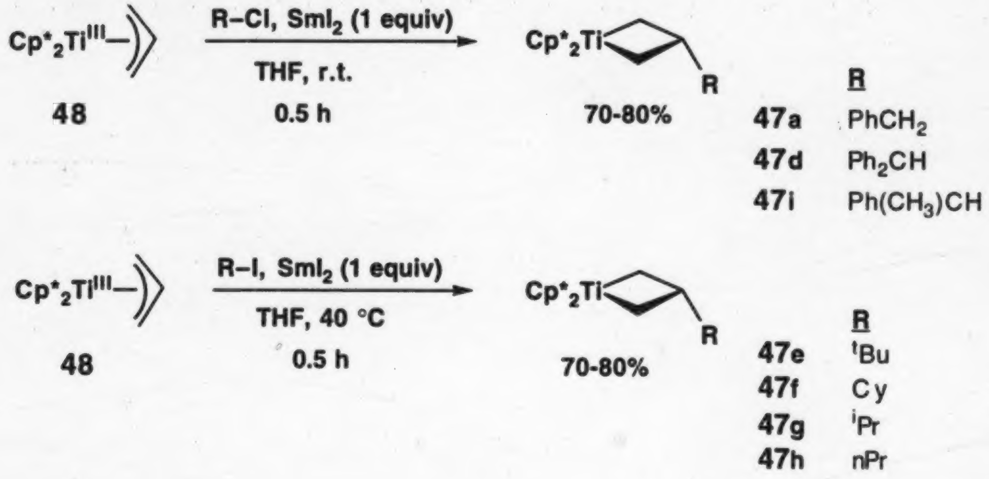

Cp*2TiCl
(49)
R–Cl, THF
-35 °C → r.t.
Cp*2Ti
R
+
Cp*2TiCl2
50
R
47a PhCH2 (88%)
47c tBu (~40%)
47d Ph2CH (94%)
Cp*2TiIII
48
Ph6Sn2
R–X, hν, 0 °C
Cp*2Ti
R
+
Cp*2Ti
X
R
47b
I 47f Cy 2 : 1
Br 47f Cy (70%) –
Cl 47g iPr (73%) –

and is attributed to the difficulty associated with generating non-activated radicals using complex **49**. Generation of secondary radicals, using photolytic decomposition of hexaphenyldistanane in the presence of an alkyl halide, enables successful alkylation of allyl complex **48**. With cyclohexyl iodide as a secondary radical precursor, a mixture of β-cyclohexyl- and β-allyl-titanacyclobutane complexes, **47f** and **47b**, are observed. Better selectivity is obtained with the corresponding cyclohexyl bromide (Scheme 1.15). Presumably, the formation of the β-allyl titanacyclobutane complex **47b** results from the decomposition of the unstable titanium allyl iodide intermediate, formed from direct oxidation of allyl complex by cyclohexyl iodide. It is reported that replacing organic halides with alkyl mercury salts or dialkyl mercury compounds results in a marginal improvement in the scope of the alkylation reaction.[39,42] However, $[Cp_2TiCl]_2$, known to generate organic free radicals with alkyl halides,[43,44] is not compatible with allyl complex **48**.

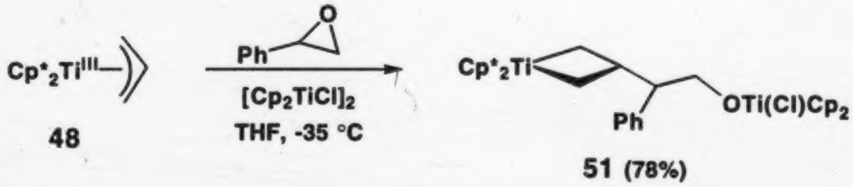
A very general and synthetically practical methodology for free radical alkylation of π-allyl complex **48**, using SmI_2•THF and organic halides, is also reported by Casty and Stryker.[39,42] Using this strategy, organic free radicals possessing varying steric profiles are generated which subsequently add to the central carbon of the η^3-allyl ligand in complex **48**, giving the β-substituted titanacyclobutane complexes **47a, 47d-i** in good to excellent yields (Scheme 1.16). For the benzylic cases, the use of low temperature and the less reactive chloride is necessary to inhibit both SmI_2-induced organic radical dimerization and competitive reaction of the organic halide with the titanocene allyl complex. For alkyl halides, the use of the iodide and higher temperature is required to provide central carbon alkylation products efficiently (Scheme 1.16).

Further, an additional radical generating strategy is shown to provide access to functionalized titanacyclobutanes.[39,42] Titanium(III)-mediated epoxide opening reaction

Scheme 1.16


Cp*$_2$Ti^{III}
48
R–Cl, SmI$_2$ (1 equiv)
THF, r.t.
0.5 h
Cp*$_2$Ti
R
70-80%
R
47a PhCH$_2$
47d Ph$_2$CH
47i Ph(CH$_3$)CH
Cp*$_2$Ti^{III}
48
R–I, SmI$_2$ (1 equiv)
THF, 40 °C
0.5 h
Cp*$_2$Ti
R
70-80%
R
47e ^{t}Bu
47f Cy
47g ^{i}Pr
47h nPr

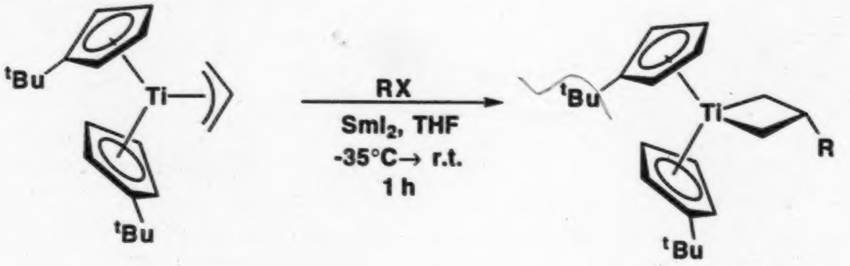
generates β-oxyalkyl radicals,[45-48] which successfully add to allyl complex **48** to give oxygen-containing titanacyclobutane complexes in modest yield, as the example in Equation 1.2 shows.


Cp*$_2$Ti^{III}
48
O
Ph
[Cp$_2$TiCl]$_2$
THF, -35 °C
Cp*$_2$Ti
Ph
OTi(Cl)Cp$_2$
51 (78%)

(1.2)

Interestingly, central carbon alkylation reactivity is not observed when $Cp_2Ti(\eta^3\text{-}C_3H_5)$ **52** is treated with SmI_2 and an alkyl halide, primarily decomposition products are obtained.[39] The slightly more electron rich $(t\text{-}BuCp)_2Ti(\eta^3\text{-}C_3H_5)$ **53**, however, successfully undergoes alkylation, as shown by its reactions with both benzyl and isopropyl radicals (Scheme 1.17). These observations strongly suggests that there is a minimum electron density requirement for central carbon alkylation: perhaps high electron density at the metal center destabilizes the singly occupied metal orbital, facilitating d→π* back-bonding into the π*-orbital of the allyl ligand. The consequences of enhanced back-bonding are an increased preference for η^3-coordination and a greater delocalization of the odd-electron density onto the central carbon of the allyl ligand, activating the complex toward radical alkylation and enhancing the central carbon regioselectivity.

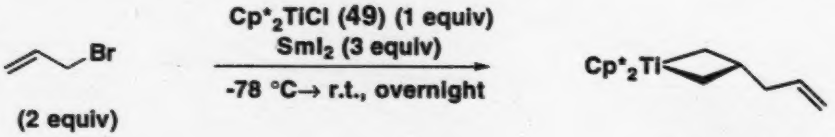
Scheme 1.17


tBu
Ti
tBu
RX
SmI2, THF
-35°C→ r.t.
1 h
tBu
Ti
R
tBu

53

	R
54a	Bn (90%)
54b	^{i}Pr (55%)

Recent unpublished reports from the Stryker group establish that generation of titanocene π-allyl complexes can be accomplished *in situ* using the SmI_2 methodology and allyl halides.[49] Thus, the reaction mixture containing Cp^*_2TiCl **49**, allyl bromide

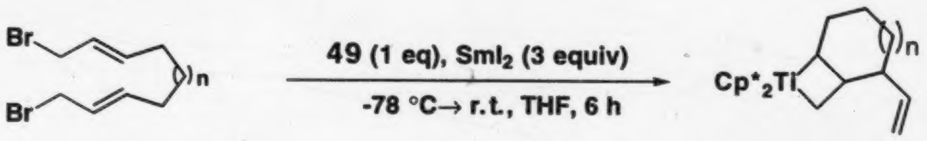

Br
(2 equiv)
Cp*2TiCl (49) (1 equiv)
SmI2 (3 equiv)
-78 °C→ r.t., overnight
Cp*2Ti

(1.3)

47 b (90%)

and samarium(II) iodide in a ratio of 1 : 2 : 3 produces β-allylmetallacycle **47b** in excellent yield (Equation 1.3).[49] This reaction, however, is not successful using crotyl bromide. An intramolecular version of this one-pot reaction has been demonstrated. In the presence of complex **49** and SmI_2, nine- and ten-carbon diallyl dibromide substrates give bicyclic titanacyclobutane complexes **55** and **56**, however, the eleven-carbon analogue fails to yield the corresponding titanacyclobutane (Scheme 1.18). The low yield of complex **56** and the failure of the eleven-carbon diallyl substrate to yield any bicyclic product possibly reflect unfavorable steric interactions between the larger carbon chains and the pentamethylcyclopentadienyl rings in the titanocene allyl intermediate. It is also

Scheme 1.18



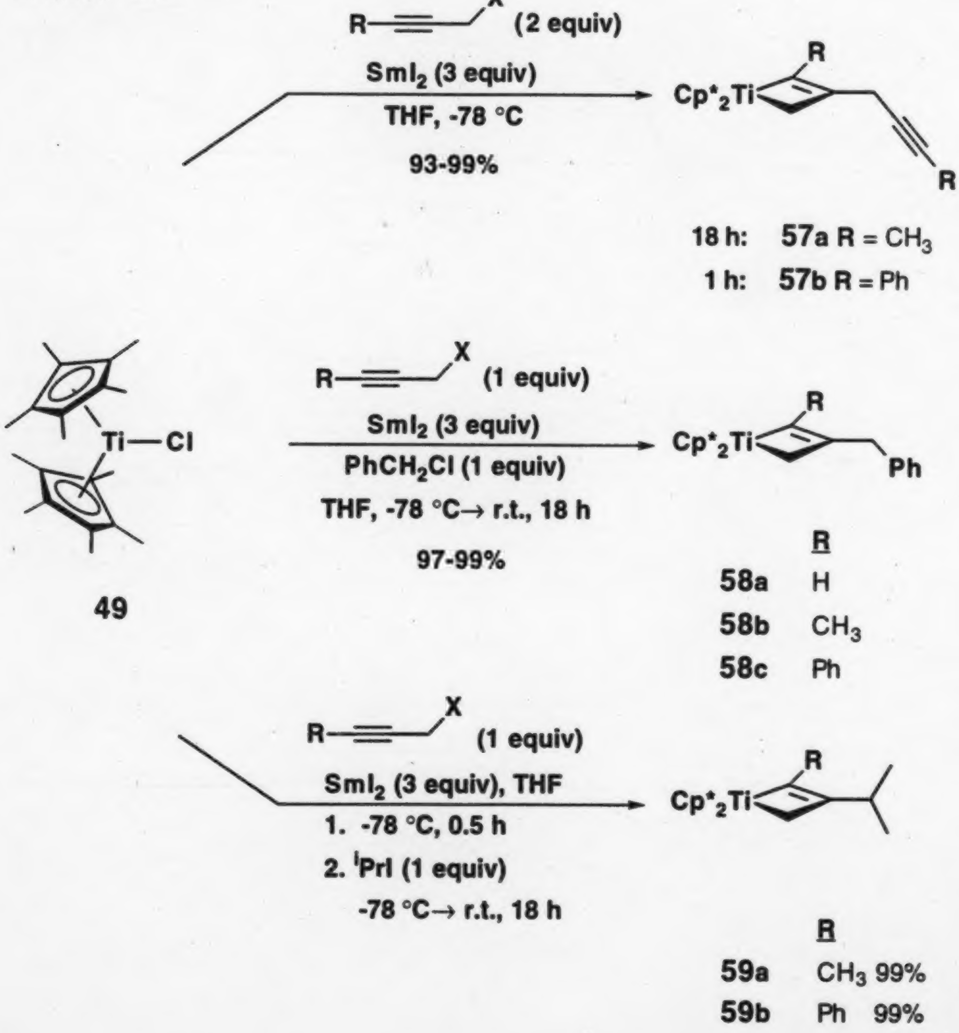
n = 1, 2, 3

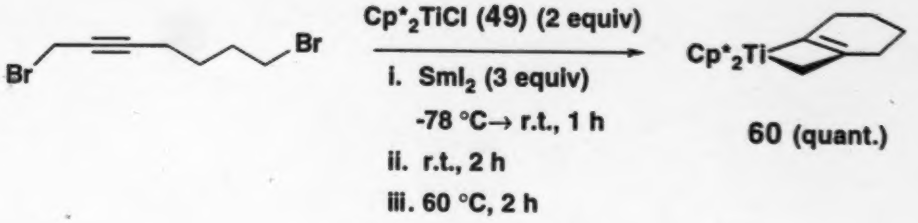
55 (n = 1, 90%)
56 (n = 2, ≤ 40%)

possible that coupling of the organic radicals resulting from the ten- and eleven-carbon diallyl dibromide substrates becomes the dominant reaction pathway. Despite this limitation, the intramolecular bicyclizations reveal the potential of this methodology for the rapid construction of fused carbocyclic rings of synthetic interest.

The potential and scope of the central carbon radical alkylation have been recently expanded to several titanium(III) η^3-propargyl complexes (Scheme 1.19).[50] It is reported that a mixture containing permethyltitanocene(III) chloride complex **49**, a propargyl halide and SmI_2, in a ratio of 1 : 2 : 3, yields exclusively the β-substituted titanacyclobutene complexes **57a** and **57b** (Scheme 1.19). The η^3-propargyl complexes, generated *in situ*, can also be trapped with other alkyl radicals generated from SmI_2-mediated halide abstraction, providing a convenient one-pot synthesis of many 2,3-disubstituted titanacyclobutene complexes (Scheme 1.19). Intramolecular alkylation with unsymmetrical propargyl alkyl dihalides is also successful, leading to the formation of synthetically attractive bicyclic products such as **60** (Equation 1.4). The generality and controlled regioselectivity of this metallacyclobutene synthesis is in contrast with titanacyclobutene synthesis via titanium alkylidene/alkyne [2 + 2] cycloaddition, the only other methodology available for preparation of this class of complexes. This latter approach fails for terminal alkynes and usually gives mixtures of regioisomers with disubstituted alkynes.[51-57]

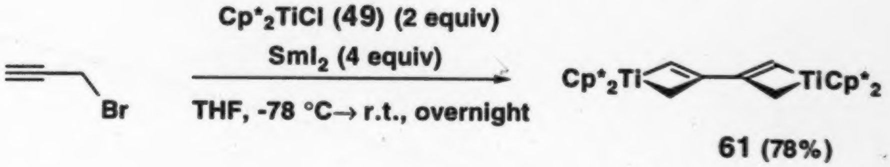
Scheme 1.19


R
X
(2 equiv)
SmI2 (3 equiv)
THF, -78 °C
93-99%
Cp*2Ti
R
R
18 h: 57a R = CH3
1 h: 57b R = Ph
Ti—Cl
49
X
R
(1 equiv)
SmI2 (3 equiv)
PhCH2Cl (1 equiv)
THF, -78 °C→ r.t., 18 h
97-99%
Cp*2Ti
R
Ph
R
58a H
58b CH3
58c Ph
X
R
(1 equiv)
SmI2 (3 equiv), THF
1. -78 °C, 0.5 h
2. iPrI (1 equiv)
-78 °C→ r.t., 18 h
Cp*2Ti
R
R
59a CH3 99%
59b Ph 99%


Br
Br
Cp*$_2$TiCl (49) (2 equiv)
i. SmI$_2$ (3 equiv)
-78 °C→ r.t., 1 h
ii. r.t., 2 h
iii. 60 °C, 2 h
Cp*$_2$Ti
60 (quant.)

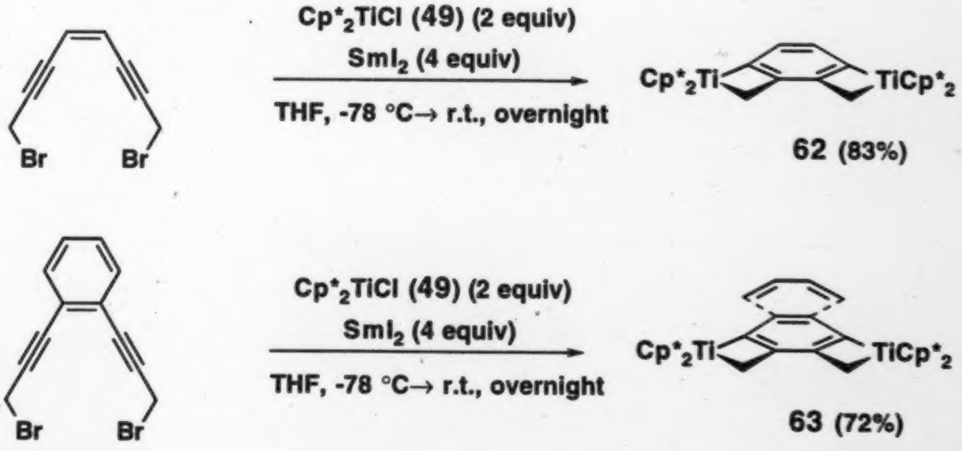
(1.4)

In contrast to the titanocene η^3-allyl complexes, the η^3-propargyl complexes seem more reactive, coupling to give dititanacyclobutene complexes.[50] As the example in Equation 1.5 illustrates, a mixture containing propargyl bromide, titanocene chloride complex **49** and SmI_2 yields complex **61** in good yield (Equation 1.5).[50] The intramolecular version of this reaction yields the intriguing dititanacyclobutene complexes **62** and **63** (Scheme 1.20). It is not yet known whether aromaticity of the product is essential to this intramolecular pseudodimerization.


Br
Cp*$_2$TiCl (49) (2 equiv)
SmI$_2$ (4 equiv)
THF, -78 °C→ r.t., overnight
Cp*$_2$Ti
TiCp*$_2$
61 (78%)

(1.5)

Scheme 1.20

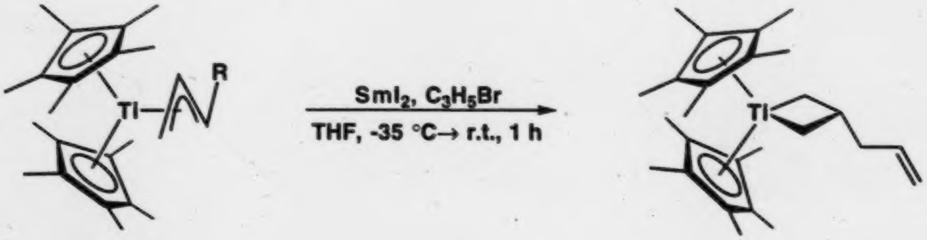

Br
Br
Cp*$_2$TiCl (49) (2 equiv)
SmI$_2$ (4 equiv)
THF, -78 °C→ r.t., overnight
Cp*$_2$Ti
TiCp*$_2$
62 (83%)
Br
Br
Cp*$_2$TiCl (49) (2 equiv)
SmI$_2$ (4 equiv)
THF, -78 °C→ r.t., overnight
Cp*$_2$Ti
TiCp*$_2$
63 (72%)

1.3. Project Goals

As a result of the potential application of central carbon alkylation as a synthetically useful carbon-carbon bond forming strategy, some effort was directed toward extending this titanacyclobutane formation to substituted π-allyl complexes. In this effort, a fundamental understanding of the structural and electronic features that govern the regiochemistry of this alkylation reaction was also sought.

Although the permethylated metallocene template is very successful at mediating central carbon radical alkylation of the η^3-allyl ligand, all attempts to extend this reaction to substituted η^3-allyl complexes failed.[58] For instance, treating titanocene complexes **64** and **65** with allyl bromide in the presence of SmI_2 resulted only in producing a low yield of β-allyl titanacyclobutane **47b** (Scheme 1.21).[58] The outcome of this reaction is presumably due to an initial preferential attack at the metal center by the allyl radical to afford a neutral Ti(IV) intermediate, which is expected to lose the more stable substituted allyl ligand as a radical. The titanium(III) allyl complex, **48**, generated, reacts in the typical manner to give titanacyclobutane **47b**. For the metal center to be alkylated in preference to the allyl ligand, we suggest that the substituted allyl ligand may be unsymmetrically coordinated, distorted towards η^3-σ,π-coordination,[34,59] or quite possibly exists in a purely η^1-coordination mode (**II**, Figure 1.5). The source of this

Scheme 1.21

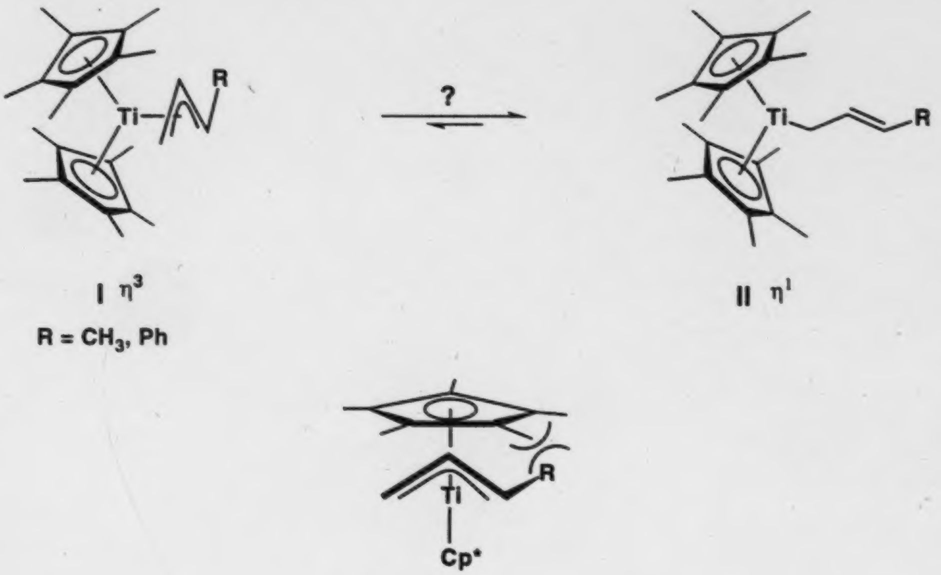


64 R = CH_3
65 R = Ph

47b

distortion away from η^3-hapticity may be an unfavorable steric interaction between the allyl substituent and the methyl groups on the cyclopentadienyl ring or the result of the weaker bond between titanium and the substituted carbon atom, or a combination of the two effects.[60] A weakening of the titanium-carbon can be attributed to destabilization of the π^*-orbital of the allyl ligand due to the presence of the substituent, the effect of which would be an attenuation of the already tenuous $d \rightarrow \pi^*$ back-bonding from a d^1 metal center. However, this argument is expected to be true only for electron donating substituents (*e.g.*, for R = Me) and since cinnamyl complex **65**, with an electron withdrawing phenyl group, also fails to give central carbon alkylation, we suggest that the unfavorable steric interaction between the substituents in the complex is probably the dominant factor inhibiting η^3-coordination and hence central carbon alkylation. As a consequence, the primary goal of the investigation described in this document is the

Figure 1.5. $\eta^3 \rightarrow \eta^1$ Equilibrium of a Titanocene(III) Substituted Allyl Complex



I η^3

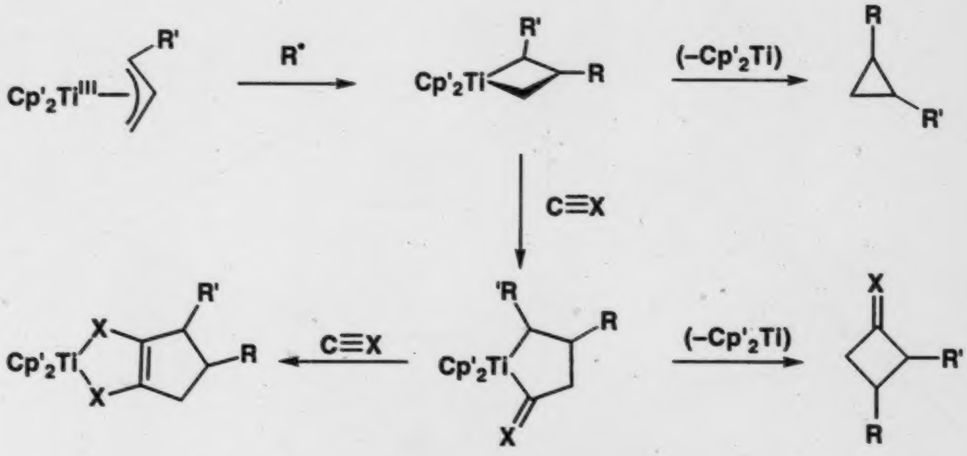
R = CH_3, Ph

II η^1

development of organometallic templates that will mediate central carbon alkylation of substituted η^3-allyl complexes by organic free radicals.

Successful alkylation of substituted allyl complexes provides a critical bridge to the development of this reactivity pattern as a synthetic methodology, particularly towards expanding the intramolecular variant leading to the synthesis of bicyclic compounds . It is evident from the one successful intramolecular cyclization that this method has the potential to efficiently construct carbocycles with multiple stereogenic atoms and fused ring systems.[49,50] When this methodology is coupled with small molecule insertion chemistry of the resultant metallacyclobutanes, various ring expanded products become accessible that in turn may be converted to uniquely functionalized organic molecules subsequent to decomplexation (Scheme 1.22).

Scheme 1.22



X = O, NR" R = alkyl; R', R" = alkyl or aryl

We considered two approaches to accomplish this goal: first, to investigate the reactivity of substituted η^3-allyl complexes in sterically more relaxed systems, with more room in the wedge between the Cp rings, and second, to investigate the reactivity of substituted η^3-allyl complexes bearing ancillary ligands with strong electron donor substituents without the concomitant bulkiness of the Cp* ligands (*vide infra*).

The *ansa*-[1]-metallocene systems[61-63] were deemed viable candidates for the approach requiring sterically less congested complexes. Structural analyses of early transition metal *ansa*-[1]-metallocene complexes show that the D(1)-M-D(2) angle (where D(1) and D(2) denote the centroids of the Cp ring system) is much smaller than those of the unbridged metallocenes.[62,64] A consequence of this is a larger space in the wedge between the cyclopentadienyl rings, making it possible for ligands with larger steric profiles to be accommodated without a concomitant increase in unfavorable steric interactions. This is especially relevant for our purposes since a substituted η^3-allyl ligand could be accommodated without any ensuing steric interactions. One important point to note about these *ansa* metallocene complexes is that pinning back the cyclopentadienyl rings results in re-hybridization of the metal center, modifying the topology of the frontier molecular orbitals,[64,65] and this could elicit unique and perhaps unfavorable reactivities with organic radicals as compared to unbridged analogues.

In the alternative approach, we examined the reactivity of substituted η^3-allyl complexes bearing ancillary ligands with strong electron donor substituents and reduced steric demand compared to the Cp* system. To achieve this, complexes with ancillary ligands in which the electronic character is modified via inductive and/or mesomeric effects without an increase in steric profile were targeted for this investigation. Strong donor ligands should increase the electron density at the transition metal, facilitating $d \rightarrow \pi^*$ back bonding to the substituted π-allyl ligand and encouraging η^3-coordination, a minimum requirement for central carbon alkylation. This strategy thus allows for tuning the organometallic template, both electronically and sterically, to facilitate inter- and intramolecular radical alkylation reactions.

Metallocenes with donor heteroatoms (nitrogen and oxygen atoms) directly bonded to the cyclopentadienyl ring were considered the best ligand candidates for this study. Not much is known of the relatively rare amino- and alkoxy-substituted metallocene complexes,[66-77] however, recent reports on structural and electrochemical properties of aminometallocene complexes of both early and late transition metal show that the nitrogen lone pair indeed interacts strongly with the cyclopentadienyl ring. In particular, the carbon-nitrogen bond distance determined for some of these complexes occur between 132.5 pm (for a Zr(IV) complex)[66] and 140.0 pm (for Co and Fe complexes),[69] consistently shorter than the typical $C(sp^2)$–N single bond length of 142.6 pm,[78] and clearly indicative of multiple bond character. More compelling are large anodic shifts, between +610 and +760 mV, observed for aminoferrocene and aminocobaltocene complexes in cyclic voltamograms recorded in the presence of Zn^{2+} and Co^{2+} ions, which disrupts the interaction of the nitrogen lone pair with the cyclopentadienyl ring.[68] The resulting increased electron density at the metal center is provided by the strong mesomeric effect of the nitrogen lone pair, which is expected to promote greater orbital overlap between the singly occupied metal d-orbital and the π^*-orbital of the allyl ligand by raising the energy of the metal d-orbitals. A consequence of this, we suggest, is significant delocalization of the odd-electron density onto the central carbon atom of the η^3-allyl ligand, and is expected to promote radical alkylation.

At the same time, a closer look at the cationic Ti(IV) system was undertaken to extend the scope of the nucleophilic addition reaction to other nucleophiles and to investigate the reactivity of complexes bearing substituents on the allyl ligand.

A second goal of this project was to begin an investigation into the conversion of titanacyclobutane complexes into cyclic organic compounds. Here we focused on ring expansion reactions using small polar unsaturated compounds (carbon monoxide, isonitriles, aldehydes and ketones) to convert the titanacycles into four- and five-membered carbocycles. Double insertion of CO or RNC into the metal-carbon bonds, followed by reductive cyclization is expected to give metal-coordinated five-membered carbocyclic rings, while a single insertion, followed by cyclization, should give a four-membered carbocycle (Scheme 1.22). The latter reactivity is rare for early transition metal metallacyclobutane complexes.[79,80]

CHAPTER 2. RESULTS AND DISCUSSION: CENTRAL CARBON ALKYLATION OF η^3-ALLYL COMPLEXES

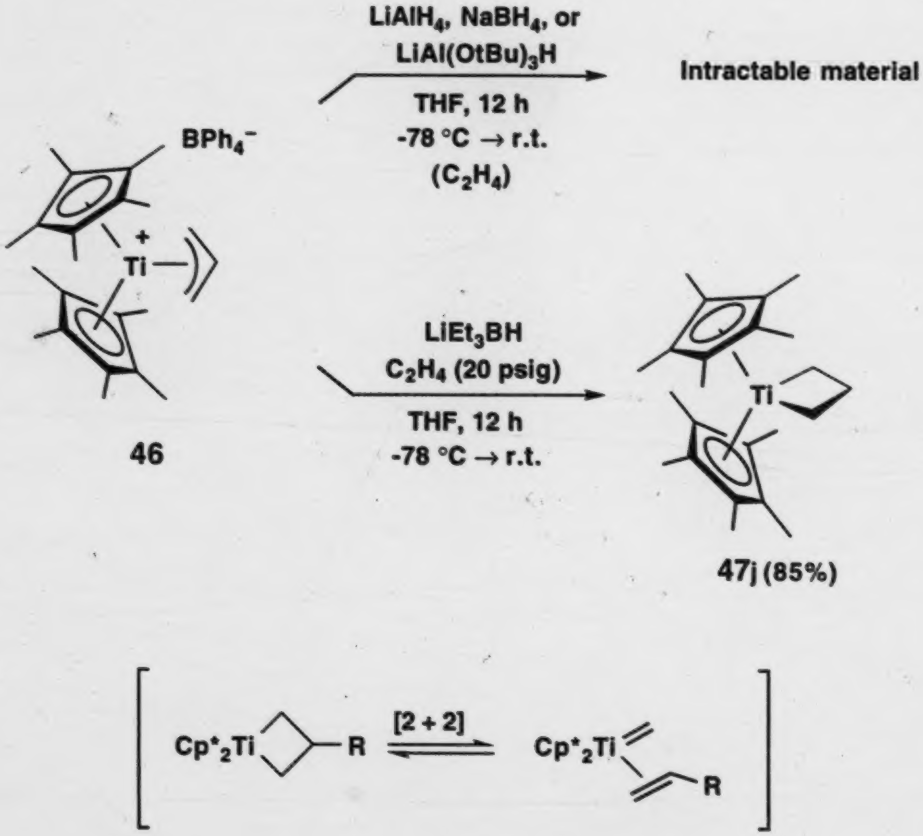
2.1. Nucleophilic Addition to Cationic Titanium(III) η^3–Allyl Complexes

In order to develop a practical carbon-carbon bond forming methodology utilizing central carbon alkylation reaction, initial efforts were directed towards extending the nucleophilic addition reactions of these Group IV cationic complexes. In a previous study, it was shown that addition to $[Cp^*_2Zr(\eta^3\text{-}C_3H_5)]^+BPh_4^-$ **43** gave either central carbon or metal alkylated adducts depending on the size of the nucleophile (Scheme 1.12, above) and as a consequence the titanium analogue, $[Cp^*_2Ti(\eta^3\text{-}C_3H_5)]^+BPh_4^-$ **46**, with a smaller metal center and lower electrophilicity, was investigated to address this issue.[81,82] Preliminary investigation of complex **46** was limited to stabilized nucleophiles and enolates (Scheme 1.13, above); as such, the present investigation was focused on extending this reaction to non-stabilized nucleophiles. In addition, the extension of this reactivity to substituted η^3-allyl complexes was also addressed.

The addition of various hydride reagents to $[Cp^*_2Ti(\eta^3\text{-}C_3H_5)]^+BPh_4^-$ **46** provided some rather interesting results. The use of $LiAlH_4$, $LiAl(O\textit{t}Bu)_3H$ or $NaBH_4$ gave only intractable material upon addition to solutions of $[Cp^*_2Ti(\eta^3\text{-}C_3H_5)]^+BPh_4^-$ **46** at low temperature (Scheme 2.1). This reactivity is in contrast to that observed by M.L.H. Green using cationic $[Cp_2W(\pi\text{-allyl})]^+PF_6^-$ **1**, which gave the unsubstituted metallacyclobutane complex in high yield (Scheme 1.1, above).[1,2] However, treatment of $[Cp^*_2Ti(\eta^3\text{-}C_3H_5)]^+BPh_4^-$ **46** with a large excess (10 equivalents) of $Li(C_2H_5)_3BH$ (Super-Hydride) in THF at low temperature gave the unsubstituted titanacyclobutane **47j**, but in variable yield. Surprisingly though, conducting this reaction under an atmosphere of ethylene with just one equivalent of Super-Hydride consistently gives **47j** in high yield

(Scheme 2.1). This suggests that complex **47j** probably decomposes in solution by a [2 + 2] cycloreversion reaction, a typical reaction pathway for early transition metal metallacyclobutane complexes, to give a titanium methylidene complex and ethylene, a

Scheme 2.1

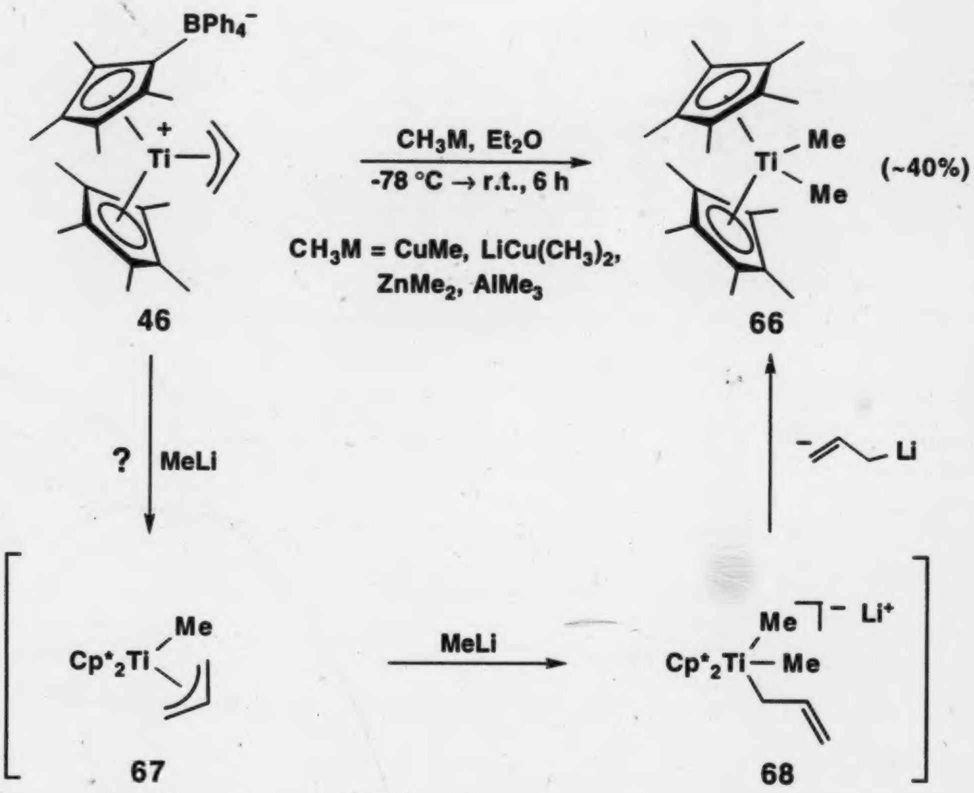

BPh$_4^-$
Ti
+
46
$LiAlH_4$, $NaBH_4$, or
$LiAl(OtBu)_3H$
THF, 12 h
-78 °C → r.t.
(C_2H_4)
Intractable material
$LiEt_3BH$
C_2H_4 (20 psig)
THF, 12 h
-78 °C → r.t.
Ti
47j (85%)
Cp*$_2$Ti
R
[2 + 2]
Cp*$_2$Ti
R

process which would be inhibited in the presence of ethylene. The same effect, however, is not observed when complex **46** is allowed to react with other hydride reagents under an atmosphere of ethylene; only decomposition products are again obtained. After isolation, complex **47j** slowly decomposes either in solution or in the solid state at room temperature, but shows little or no decomposition when stored at -35 °C for an extended period. It appears that the absence of a β-substituent promotes facile access to the transition state necessary for the [2 + 2] cycloreversion reaction, which is seen in β-substituted permethyltitanocene analogues only at much higher temperatures (> 70°C).[25,39] It is important to note that the presence of an α-substituent also adds thermal stability to titanacyclobutane complexes in the permethyltitanocene system.[83]

Although this thermal instability prevents purification by recrystallization, the identity of the unsubstituted titanacyclobutane **47j** was determined unambiguously by analysis of the spectroscopic data. The ^1H NMR spectrum shows three sets of resonances, a 30-hydrogen singlet at δ 1.66 for the Cp* methyl protons, a four-hydrogen multiplet at δ 1.13 for the α-methylene protons, and a typical upfield multiplet at δ -0.15 for the β-methylene hydrogen atoms. The ^{13}C NMR spectrum also corroborates the ^1H NMR data by showing the two types of carbon resonances for the Cp* ligands at δ 115.2 and 11.7 for the quaternary and methyl carbon atoms, respectively, and characteristic resonances for the α- and β-methylene carbon atoms at δ 73.6 and 25.1, respectively. High resolution mass spectrometry of a pure sample of **47j**, obtained by recrystallization in cold pentane, confirms its elemental composition.

Nucleophilic addition of the larger methyl anion exhibits rather surprising regioselectivity. In an initial study, cationic allyl complex **46** gave only $Cp^*_2TiMe_2$ **66**[84] upon treatment with methyllithium or methylmagnesium chloride, both hard methyl anion reagents.[25,39] It was thought that treating complex **46** with soft methyl nucleophiles, such as lithium dimethylcuprate or methylcopper, might yield the expected central carbon alkylation product. In any event, however, either reagent gave dimethyl complex **66** as the only product observed, as previously reported (Scheme 2.2).[25,39] Two other sources of nucleophilic methyl, dimethylzinc and trimethylaluminium, also failed to give central carbon alkylation. It is conceivable that the formation of complex **66** results from initial

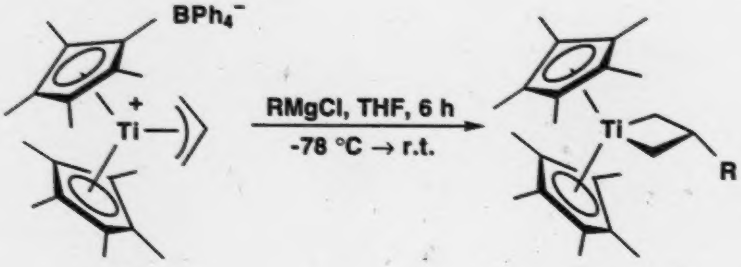
Scheme 2.2


BPh$_4^-$
Ti
+
46
CH$_3$M, Et$_2$O
-78 °C → r.t., 6 h
CH$_3$M = CuMe, LiCu(CH$_3$)$_2$, ZnMe$_2$, AlMe$_3$
Ti
Me
Me
(~40%)
66
?
MeLi
Li
Cp*$_2$Ti
Me
67
MeLi
Me
Li$^+$
Cp*$_2$Ti
Me
68

metal alkylation followed by loss of the allyl moiety as outlined in Scheme 2.2, but this result is not understood. Two previous investigations reported similar reactivity using analogous Ti(IV) complexes (Cp*$_2$Ti(R)Cl (R = *n*Pr, -CH=CH$_2$) upon treatment with methyl anion.[85,86]

Greater success was achieved with other non-stabilized carbon nucleophiles. Thus, addition of either isopropyl or *tert*-butyl Grignard reagents to cold THF solutions of complex **46** gave the corresponding β-substituted metallacycles in high yield (Scheme 2.3). The efficiency of these reactions was comparable to reactions of **46** with the stabilized nucleophiles, as previously reported.[25,39] Unlike the unsubstituted metallacyclobutane complex **47j**, these complexes have thermal stability similar to the other substituted analogues (Schemes 1.14 and 1.15), decomposing only when heated above 70 °C.[25,39]

Scheme 2.3



46

	R
47e	^{t}Bu (75%)
47g	^{i}Pr (80%)

Analysis of the spectroscopic data of the β-*tert*-butyltitanacyclobutane **47e** and comparison to an authentic sample[42] confirmed the identity of this complex. The ^{1}H NMR spectrum shows a four-hydrogen multiplet at δ 0.23 and an upfield one-hydrogen multiplet at δ -0.28, assigned to the α-methylene and β-methine hydrogen atoms, respectively, of the four-membered ring. The *tert*-butyl group is identified by the singlet at δ 1.06, while the methyl groups on the inequivalent Cp* ligands are denoted by the singlets at δ 1.79 and 1.65. Further support for the assignment of **47e** comes from analysis of the ^{13}C NMR spectrum which shows signals for the α-methylene and β-methine carbon atoms at δ 61.7 and 27.7, respectively. In addition, the inequivalent Cp* ligands are indicated by the two signals at δ 119.0 and 118.1 for the quaternary carbons, and the resonances at δ 12.4 and 11.4 for the methyl groups. The remaining resonances in the spectrum are assigned to the *tert*-butyl substituent and are found at δ 35.1 and 29.6 assigned to the quaternary carbon atom and the carbons of the methyl groups, respectively. Comparison of this spectral data with the previously reported β-*tert*-butyltitanacyclobutane complex confirmed the identity of complex **47e**.[42] The structural assignment of **47g** also follows from the analysis of the spectral data, and comparison with an authentic sample.[42]

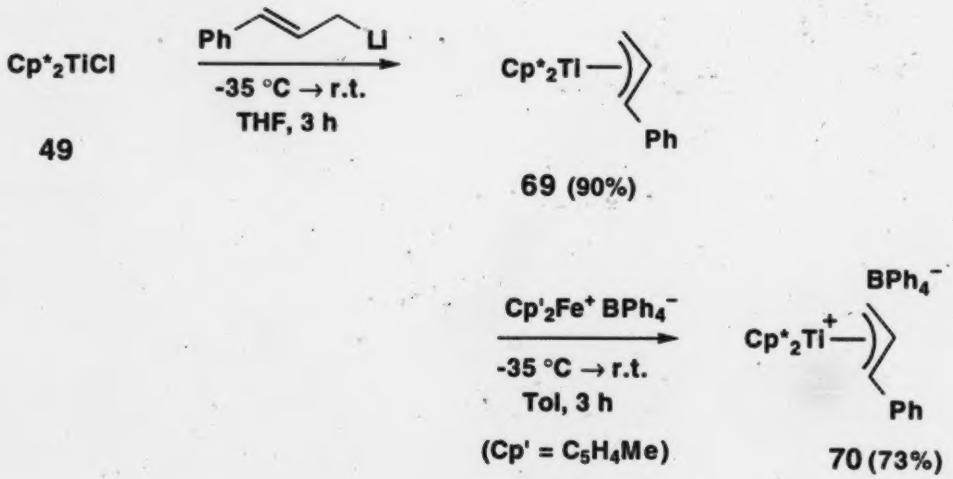
It is instructive to note that the direct C-H coupling constant for the carbon atoms in the titanacyclobutane ring is about 8 Hz higher than expected for simple sp^3-hybridized carbon atoms. Presumably, this reflects the level of ring strain in the four-membered metallacycle; ring strain increases the per cent s-character of the C-H bond and hence the associated coupling constant.[87] Additionally, even though the ^{1}H NMR resonance for the β-proton always appears characteristically upfield (between -1.0 and 0.0 ppm), increased branching in the β-substituent deshields this signal.[42]

Attempts to extend the nucleophilic addition reaction to other nucleophiles, such as sp^2-hybridized anions (*i.e.*, phenyl), were met with disappointment. The lack of central carbon alkylation of some nucleophiles reflects the subtlety in the reactivity of this complex and does not bode well for general synthetic applications.

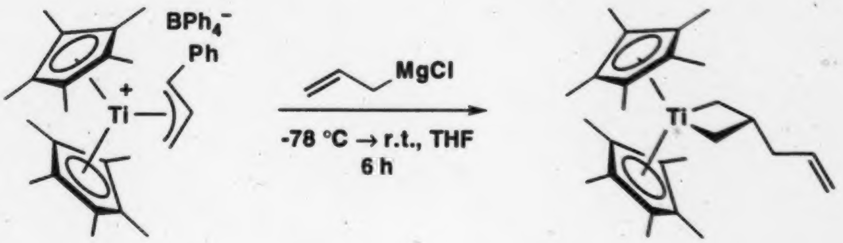
2.2. Nucleophilic Addition to Cationic Ti(IV) Cinnamyl Complex

Extending the nucleophilic addition reaction to substituted η^3-allyl complexes was sought by using the cationic cinnamyl complex $[Cp^*_2Ti(\eta^3\text{-}C_3H_4Ph)]^+BPh_4^-$ **70**. The synthesis of complex **70** started with the preparation of Ti(III) complex **69** by a procedure analogous to that used for the synthesis of parent cation **46** (Scheme 2.4).[88] Thus, treatment of a cold THF solution of the Cp^*_2TiCl **49** with cinnamyllithium at - 78°C, subsequently allowing the mixture to warm to room temperature, gives the burgundy Ti(III) cinnamyl complex, $Cp^*_2Ti(\eta^3\text{-}C_3H_4Ph)$, **69** in high yield (Scheme 2.4). Oxidation of this paramagnetic complex in toluene with $[Cp'_2Fe]^+BPh_4^-$ (Cp' = $C_5H_4CH_3$) gives the cationic complex $[Cp^*_2Ti(\eta^3\text{-}C_3H_4Ph)]^+BPh_4^-$ **70** in good yield after isolation from toluene by filtration. The spectroscopic characteristics of this complex are similar to cationic titanocene allyl complex **46**, although the cinnamyl ligand in this complex is highly fluxional in the ^{1}H NMR spectrum even at temperatures as low as -100 °C. At room temperature, only resonances for the Cp* ligands (δ 1.99) and phenyl groups of both the tetraphenylborate counter ion and cinnamyl ligand (overlapping multiplets at δ 7.55) are readily observed. At -100 °C, however, the spectrum shows broad multiplets at δ 6.44, 6.32, 6.15, 5.08, 5.06, 4.16 and 3.45, in addition to the previously observed signals, indicating the presence of two species which are slowly interconverting. These species are most probably the η^3- and η^1-cinnamyl complexes and would account for the seven multiplets, tentatively assigned to the allylic hydrogen atoms.

Scheme 2.4



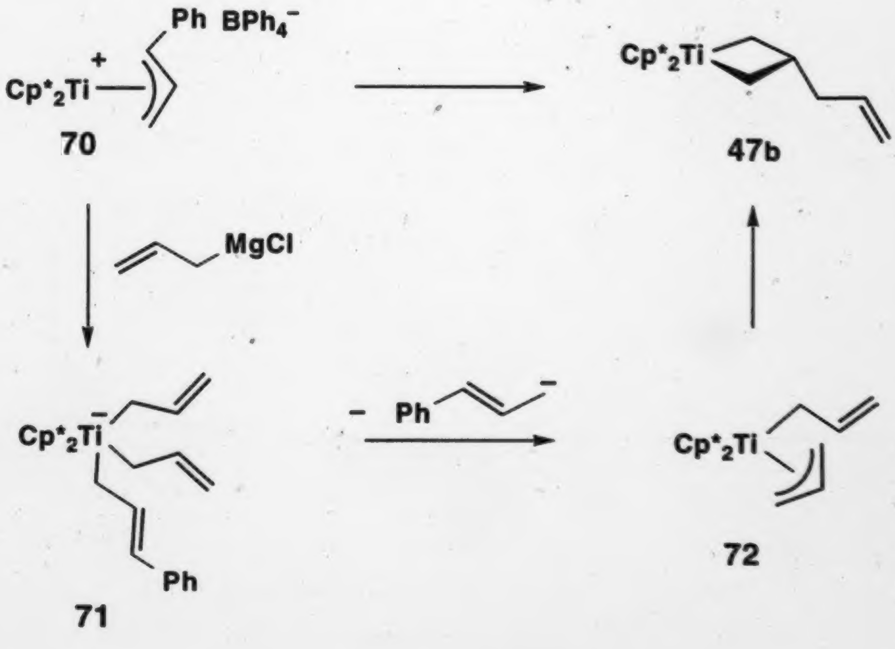
Addition of nucleophiles of varying sizes and nucleophilicities to cationic cinnamyl complex **70** yielded only complex product mixtures. For instance, addition of the potassium enolate of acetophenone, benzyl potassium or benzylmagnesium chloride gave only intractable product mixtures, which appear to contain dimers of the organic cinnamyl radical. Addition of methyllithium or methylmagnesium chloride gave only the known complex $Cp^*_2TiMe_2$ **66**. A product mixture containing the β-allyl metallacycle **47b** and the cinnamyl radical dimer is obtained when complex **70** is treated with allylmagnesium chloride (Equation 2.1). This latter observation suggests that the allyl


BPh4−
Ph
+
Ti
MgCl
-78 °C → r.t., THF
6 h
Ti

(2.1)

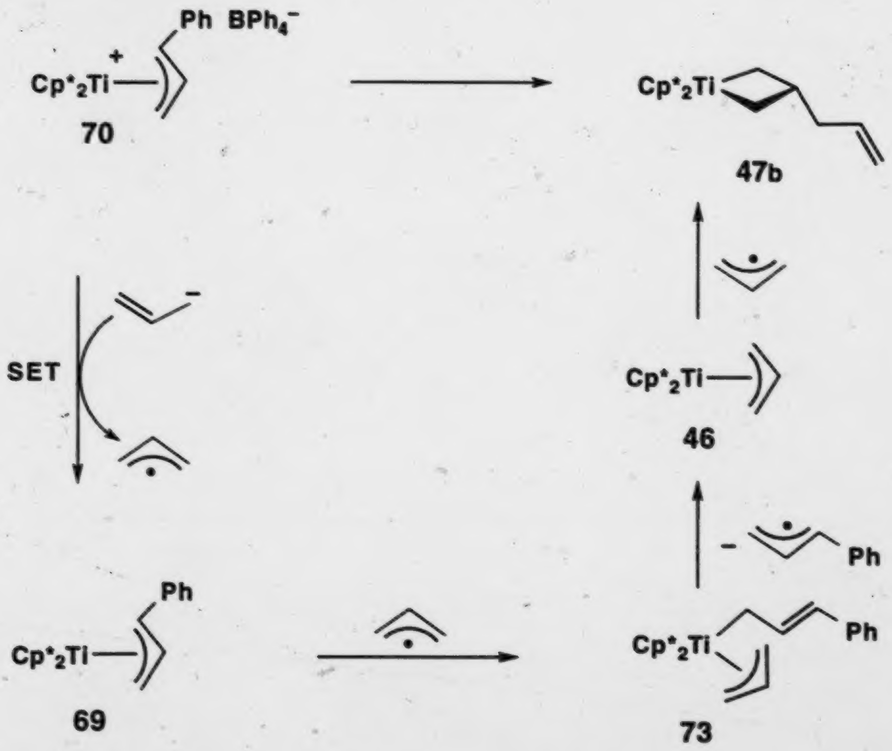
70 **47b (30%)**

Scheme 2.5

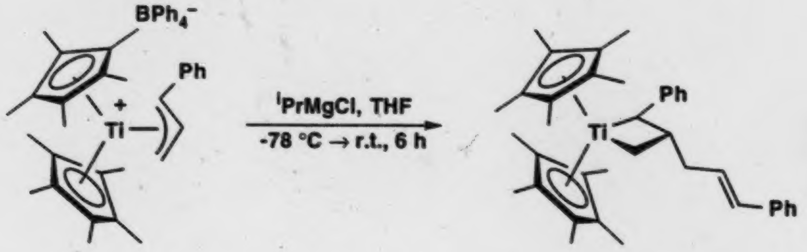

Ph BPh4−
+
Cp*2Ti
70
Cp*2Ti
47b
MgCl
−
Cp*2Ti
Ph
71
− Ph
−
Cp*2Ti
72

nucleophile attacks at the metal center instead of the central carbon of the cinnamyl ligand, giving an intermediate bis(allyl)cinnamyltitanate complex **71** (Scheme 2.5). This latter species then loses the more stabilized cinnamyl anion to form the bisallyl complex **72**, which can then be transformed to complex **47b**, possibly by allyl radical rearrangement as observed in the analogous zirconium system.[41] This Scheme, however, does not account for the formation of cinnamyl dimers. An alternative rationalization requires loss of the cinnamyl ligand from an intermediate allyl(cinnamyl)titanium complex **73** as a free radical (Scheme 2.6). However, to obtain allyl radical for alkylating the Ti(III) allyl complex, a single electron transfer process must occur between the allyl anion and the titanium(IV) complex **70**, which is reduced to the d^1 Ti(III) cinnamyl complex **69**. The subsequent sequence of radical exchange steps from complex **73** could account for the formation of β-allyltitanacyclobutane **47b**.

Scheme 2.6



A reactivity pattern similar to allylmagnesium chloride is seen when complex **70** is treated with isopropyl magnesium chloride at low temperature (Equation 2.2). This reaction gives a complex product mixture containing a titanacyclobutane complex, tentatively assigned as 3-cinnamyl-2-phenylbis(pentamethylcyclopentadienyl)-titanacyclobutane **74**. The formation of titanacyclobutane complex **74** can be explained by a rationalization analogous to that used for complex **47b**. As a result of the low yield and the multitude of inseparable products from this reaction, complete structural assignment of complex **74** has not been possible. However, the ^{1}H NMR spectrum reveals characteristic upfield resonance of a β-methine hydrogen atom at δ -0.33 ppm and singlets at δ 1.76 and 1.62 for the inequivalent Cp* ligands. It is clear that the known β-isopropyl metallacycle is not formed in this reaction, primarily because of the absence of two methyl doublets in the ^{1}H NMR spectrum (~ 1.2 ppm) for the diastereotopic methyl groups of the isopropyl substituent.



70 **74** (low yield) (2.2)

From these observations, it seems that the primary reaction pathway of cationic cinnamyl complex **70** is initial attack at the metal center followed by loss of the cinnamyl ligand. These results suggest that the cinnamyl ligand exists mostly in an η^1-coordination mode, exposing the metal center to attack by nucleophiles. As discussed, unfavorable steric interactions between the methyl groups on the cyclopentadienyl rings and the phenyl substituent on the cinnamyl ligand may disfavor η^3-coordination.

Since stabilization of the titanocene cation depends critically on the electron-richness of the complex, eliminating the Cp* ligands did not appear to be an attractive approach to circumvent the steric problem. Furthermore, with no back-bonding from the d^0-metal center to the substituted allyl ligand, there is little chance to exert any direct electronic influence on the hapticity of the allyl ligand. As a consequence, the d^1 titanocene allyl complexes seemed to be the most logical substrates to successfully extend the central carbon alkylation reaction. In addition, the neutral d^1 Ti(III) complexes can more easily be made and used *in situ*, an important consideration for making this reaction a useful carbon-carbon bond forming process in organic synthesis.

2.3. Radical Addition to Neutral η^3-Allyl Complexes

2.3.1. Introduction

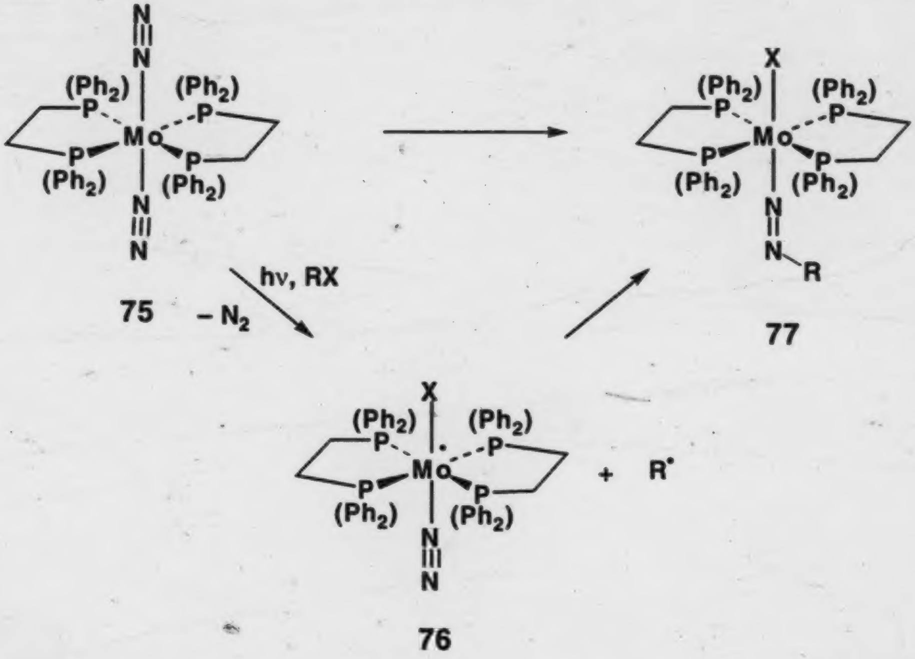
There are numerous synthetically important organic transformations involving organic ligands coordinated to transition metals, however, direct addition of organic free radicals to unsaturated hydrocarbon ligands is a virtually undeveloped field. This area has remained relatively unexplored despite the plethora of transition metal based methodologies developed to initiate otherwise purely organic free radical reactions.[89] The development of such methodology in principle unites the unique reactivity of organic free radicals with the range of control elements inherent in transition metal templated reactions. This has the potential to extend greatly the repertoire of selective carbon-carbon bond forming reactions useful for constructing important and complex organic compounds.

There are several reports of radical addition reactions to non-hydrocarbyl ligands, particularly N_2 and NO.[90-93] Relatively fewer examples of radical addition to coordinated hydrocarbyl ligands are known. One well-studied example of the former is the addition of organic radicals to a coordinated dinitrogen ligand in low valent complexes of molybdenum and tungsten.[90] For example, the photolysis of bis(dinitrogen) molybdenum complex **75** in the presence of alkyl halide results in the formation of the alkyl diazenido complex **77** (Scheme 2.7). This chemistry has been extended to synthesis and can be used to insert nitrogen into organic frameworks.[94]

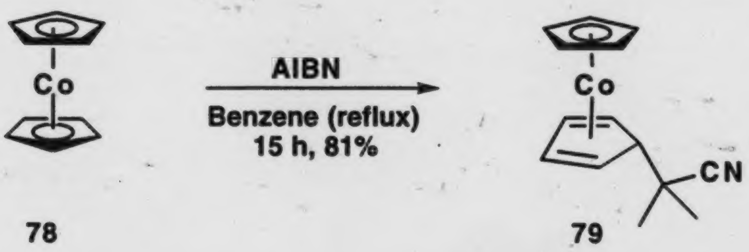
Perhaps the first direct investigation of radical addition to a transition metal coordinated hydrocarbyl ligand is reported by Schwartzer.[95] In this investigation, the thermal decomposition of AIBN in the presence of the 19-electron complex $(C_5H_5)_2Co$

78 produces the corresponding cyclopentadienyl-[5-*exo*-(1-cyano-1-methylethyl) cyclopentadiene]cobalt complex **79** in high yield (Equation 2.3). This observation, along

Scheme 2.7


N
N
(Ph2)
(Ph2)
P
P
Mo
P
P
(Ph2)
(Ph2)
N
N
75
hν, RX
– N2
X
Mo
N
N
R
77
X
Mo
N
N
76
+ R•

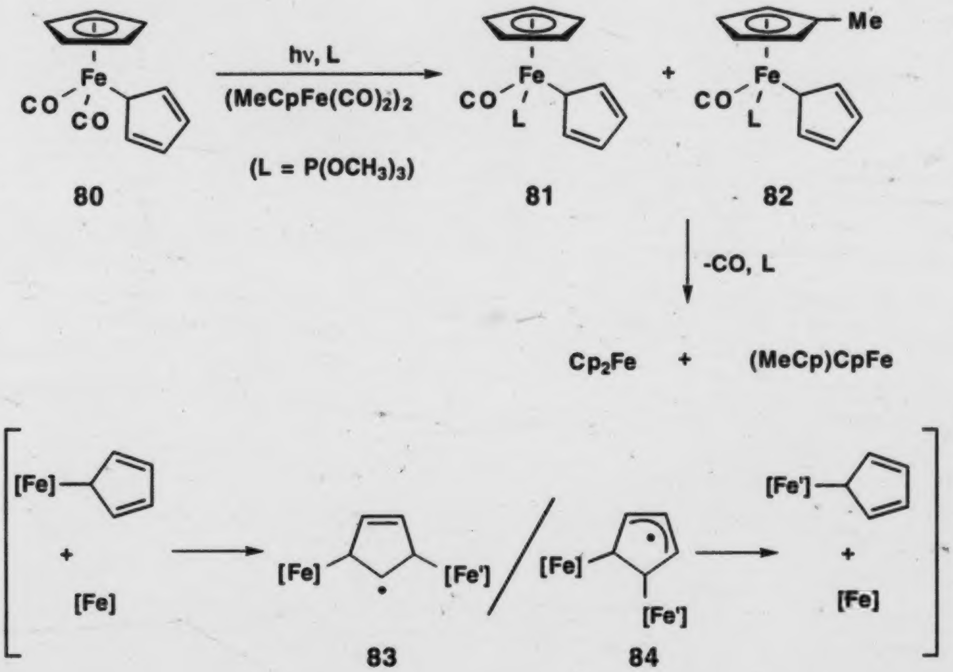
with a radical-clock investigation of the 19-electron sandwich complexes, unequivocally established the involvement of free radicals in previously studied reactions of halocarbons with 19-and 20-electron metallocene and bis(η^6-arene) complexes.[96-101]


Co
AIBN
Benzene (reflux)
15 h, 81%
Co
CN
78
79

(2.3)

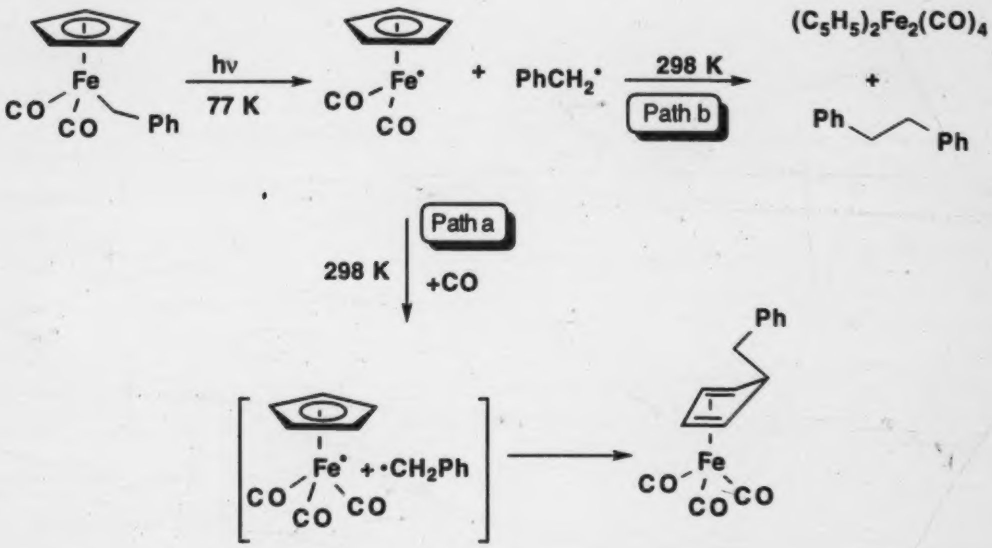
In addition, radical addition/elimination pathways have been defined for the reactions of η^1-cyclopentadienyl and η^1-allyl complexes with both organic and metal-centered radicals.[102-106] For example, photolysis of $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)Fe(CO)_2$ **80** in the presence of $[(\eta^5\text{-}C_5H_4CH_3)Fe(CO)_2]_2$ and $P(OCH_3)_3$ gives a mixture of ferrocene and methylferrocene resulting from a radical mediated exchange of the Cp ligand between metal centers (Scheme 2.8). This ligand transfer reaction can occur by an addition-elimination sequence involving species such as **83** or **84**.[102]

Scheme 2.8



Particularly interesting is the migration of the benzyl ligand from the metal to Cp observed upon photolysis of $(C_5H_5)Fe(CO)_2CH_2Ph$.[105] The outcome of this reaction is dependent on the presence or absence of carbon monoxide: under CO, the η^4-$(PhCH_2C_5H_5)Fe(CO)_3$ adduct is formed (Scheme 2.9, path a), while in the absence of CO, only dimers of both the organometallic and organic radicals are observed (Path b).[105]

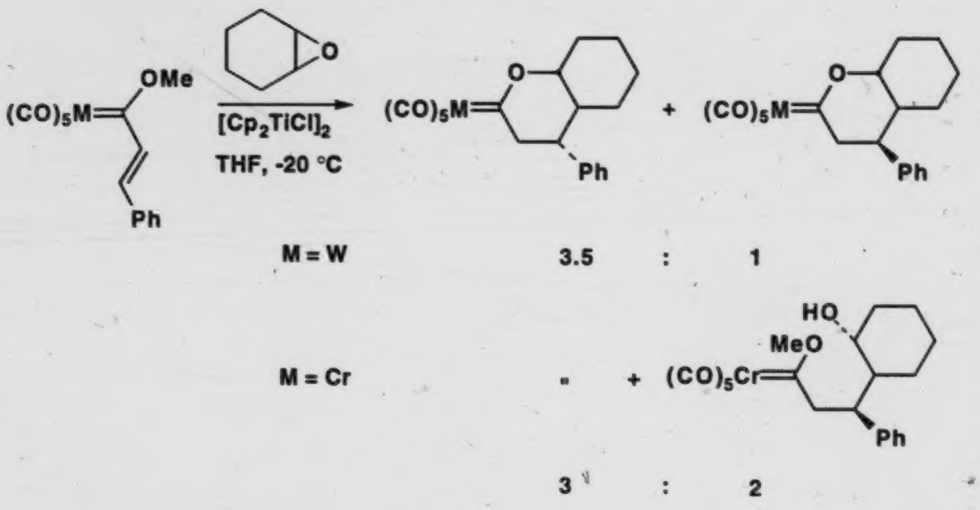
Scheme 2.9



The only significant attempt to develop radical addition to transition metal templated hydrocarbyl ligands from an organic perspective has been reported by Merlic and Xu.[107] In this investigation, α,β-unsaturated Fischer carbene complexes are treated with β-alkoxy alkyl radicals to produce substituted pyrans in moderate yields and modest diastereoselectivities (Scheme 2.10). The reaction proceeds by addition of a β-alkoxy alkyl radical, generated by Ti(III) epoxide opening, to the uncomplexed vinyl group of an unsaturated carbene complex, followed by trapping of the resulting delocalized carbene α-radical by a second equivalent of titanocene(III) chloride. In this reaction, the transition metal carbene plays a role analogous to that of organic acrylate esters in typical radical conjugate addition reactions.[45-47,108,109]

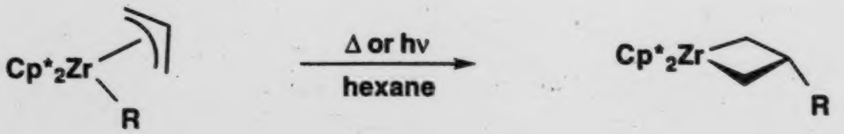
In work from the Stryker group, a very interesting reactivity pattern was observed using $Cp^*_2Zr(\eta^3\text{-}C_3H_5)(\eta^1\text{-}C_3H_5)$ **45b** and related complexes (Scheme 2.11).[34,41] This transformation, a ligand rearrangement that can be promoted either thermally or

Scheme 2.10


OMe
(CO)5M
Ph
O
[Cp2TiCl]2
THF, -20 °C
(CO)5M
O
Ph
+
(CO)5M
O
Ph
M = W
3.5 : 1
HO
MeO
M = Cr
+
(CO)5Cr
Ph
3 : 2

photochemically, results in the formation of the β-substituted zirconacyclobutane complexes. Preliminary mechanistic investigations (principally kinetics and solvent effects) suggested a free radical pathway for this unimolecular rearrangement, with the predominant pathway via intramolecular ligand rearrangement. This is the work that engendered the first study involving the direct addition of organic radicals to titanium(III) allyl complexes, as described earlier.[39,42] Also as described previously, the principal

Scheme 2.11


Cp*2Zr
R
Δ or hν
hexane
Cp*2Zr
R

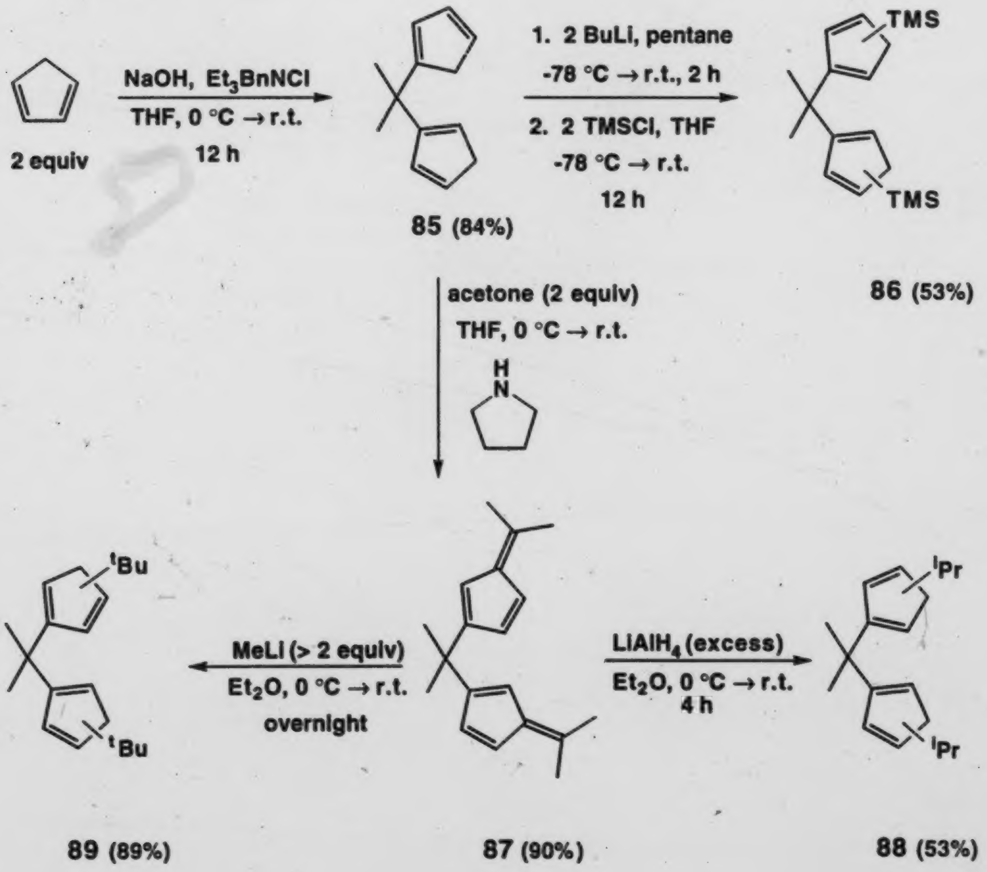
	R		R
45a	$PhCH_2$	**44a**	$PhCH_2$
45b	$CH_2CH=CH_2$	**44c**	$CH_2CH=CH_2$
45c	$CH_2CH=CHCH_3$	**44d**	$CH_2CH=CHCH_3$ (two isomers)

limitation of that work was the detrimental presence of any substituent on the allyl ligand. As a consequence, we began an investigation into the development of organometallic templates that facilitate central carbon alkylation of substituted η^3-allyl complexes with organic free radicals.

2.3.2. Synthesis of *ansa*-Bridged Titanocene η^3–Allyl Complexes

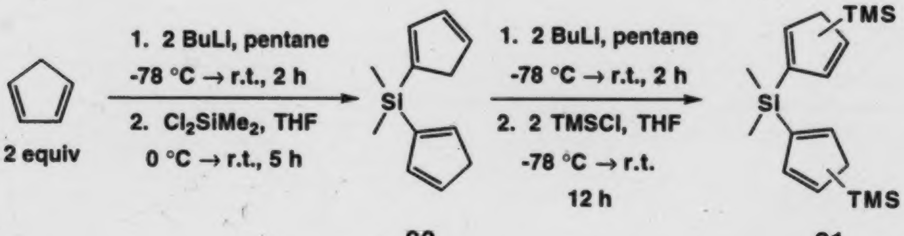
The preparation of the *ansa*-[1]-titanocene complexes required for this investigation was readily accomplished by using literature procedures, with minor experimental modification in some cases. The use of standard fulvene chemistry enabled the rapid synthesis of several one-carbon bridged dicyclopentadiene ligands, illustrated for

Scheme 2.12


2 equiv
NaOH, Et_3BnNCl
THF, 0 °C → r.t.
12 h
85 (84%)
1. 2 BuLi, pentane
-78 °C → r.t., 2 h
2. 2 TMSCl, THF
-78 °C → r.t.
12 h
TMS
TMS
86 (53%)
acetone (2 equiv)
THF, 0 °C → r.t.
H
N
tBu
tBu
MeLi (> 2 equiv)
Et_2O, 0 °C → r.t.
overnight
$LiAlH_4$ (excess)
Et_2O, 0 °C → r.t.
4 h
iPr
iPr
89 (89%)
87 (90%)
88 (53%)

compounds **85**, **86**, **88** and **89** (Scheme 2.12).[63,110] Corresponding silyl-linked biscyclopentadiene ligands **90** and **91** were prepared by alkylation of dichlorodimethylsilane with cyclopentadienyllithium (Scheme 2.13)[111-113] and further functionalized using standard silylation methodology. All of the cyclopentadiene-type compounds are obtained as a mixture of double bond isomers, from rapid thermal [1,5]-sigmatropic shifts in the cyclopentadienyl rings.

Scheme 2.13

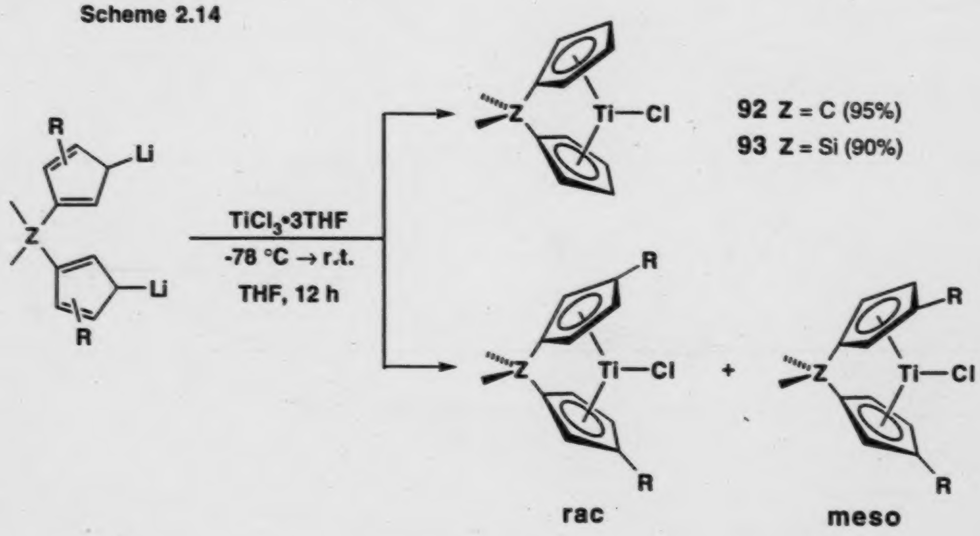


90 **91**

Scheme 2.14 outlines the synthetic sequence used to prepare both carbon and silicon *ansa*-[1]-bridged titanocene chloride complexes **92-97**, the precursors to the η^3-allyl complexes required for this investigation. Typically, the synthesis of these *ansa*-bridged titanocene(III) chloride complexes involves thoroughly mixing one equivalent each of the preformed dilithium salt of the dicyclopentadiene substrate and $TiCl_3$•3THF as solids, cooling to -78 °C, and adding cold (-78 °C) THF. The resultant solution is allowed to warm to room temperature and subsequently stirred for several hours. The yields obtained for the monochloride complexes depend on the degree of substitution of the dicyclopentadiene substrate. For unsubstituted substrates **92**, **93**, very good yields are obtained (> 90%); however, for substituted substrates **94-97** (R = TMS, ^{i}Pr, ^{t}Bu) the isolated yields are consistently lower. In addition, diastereomeric mixtures of the *rac* and *meso* stereoisomers are obtained with low selectivity (Scheme 2.14). Typically, the *meso* isomer is obtained in equal amount to the *rac* isomer or in slight excess, except for *ansa*-

[1]-bridged bis(*tert*-butylcyclopentadienyl)titanium chloride **96**, for which only the *rac* isomer is observed. Despite conducting these reactions under a variety of conditions, including those used previously for enhancing the yields and selectivities of the

Scheme 2.14



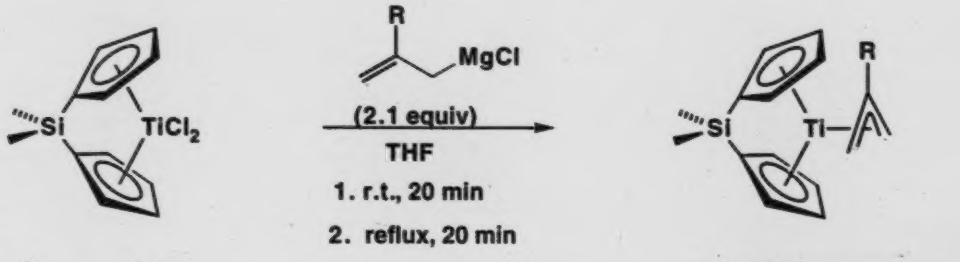
92 Z = C (95%)
93 Z = Si (90%)

	Z	R
94	C	SiMe$_3$ (18%) (2.6:1)
95		^{i}Pr (22%) (1:1)
96		^{t}Bu (40%) (*rac* only)
97	Si	SiMe$_3$ (20%) (1:1)

corresponding *ansa*-metallocene dichloride complexes,[114] no further improvement in yields or selectivities could be obtained. Purification could be accomplished by repeated cooling of the diastereomeric mixtures to - 35 °C in hexanes, followed by filtration, effecting the separation of the monochloride complexes into *meso* and *rac* isomers. In all cases, the *meso* diastereomer precipitates out first, followed by the more soluble *rac* isomer as determined by oxidation to their corresponding Ti(IV) dichloride complexes. Subsequent recrystallization gives the diastereomerically pure *ansa*-[1]-bridged titanocene(III) monochloride complexes. These paramagnetic complexes were characterized either by high resolution mass spectrometry or elemental analyses and, in some cases, by oxidization to the corresponding diamagnetic dichloride complexes, which were then characterized by the usual spectroscopic techniques.

The *ansa*-[1]-titanocene η^3-allyl complexes **98-112** are readily prepared by allylation of the corresponding *ansa*-[1]-titanocene(III) and (IV) chloride complexes (Table 2.1). As illustrated by the synthesis of complexes **102** and **103** (Scheme 2.15), the

Scheme 2.15

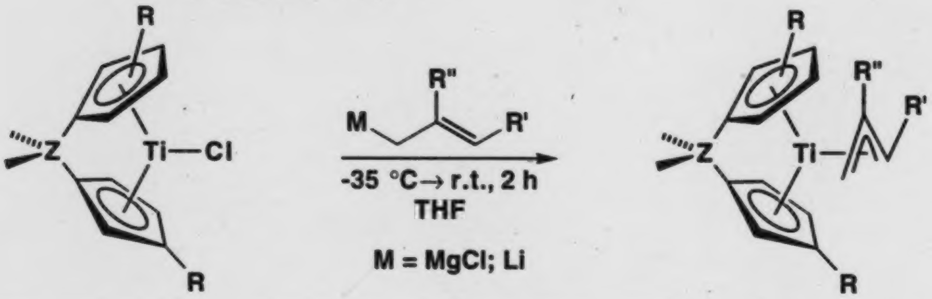


102 R = H (71%)
103 R = CH_3 (26%)

initial procedure used to prepare the allyl complexes was by treatment of the *ansa*-[1]-titanocene(IV) dichloride complex[111,112] with 2.1 equivalents of the appropriate Grignard reagent at low temperature, followed by heating the reaction mixture to reflux. The reaction proceeds by an initial reduction of the Ti(IV) dichloride complex to the trivalent titanium complex by one equivalent of the Grignard reagent, followed by alkylation with the second.[115] While this procedure offers a high yield in the case of complex **102**, a very low yield was obtained for complex **103**. A potential limitation of this procedure also is that dichloride complexes with stronger donor ancillary ligands may not undergo such facile reduction.

An alternative approach to the synthesis of these complexes was adopted, using a procedure previously developed for the preparation of $Cp^*_2Ti(\eta^3\text{-}C_3H_5)$ **48** (Table

Table 2.1. *ansa*-[1]-Titanocene Allyl Complexes from the Corresponding Monochloride Complexes



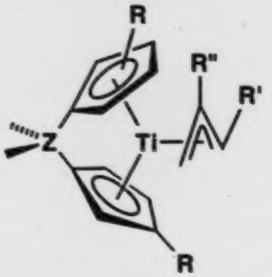
	Z	R	R'	R"	Yield (%)
98	C	H	H	H	37
99			H	CH_3	24
100			CH_3	H	72
101			Ph	H	21
102	Si		H	H	8.5 (71*)
103			H	CH_3	(26*)
104			CH_3	H	13
105-*meso*	C	$SiMe_3$	H	H	82
105-*rac*			H	H	66
106-*meso*			CH_3	H	72
106-*rac*			CH_3	H	57
107-*meso*			Ph	H	33
107-*rac*			Ph	H	83
108-*meso*	Si	$SiMe_3$	H	H	94
109-*meso*			CH_3	H	quant.
110-*meso*	C	^{i}Pr	CH_3	H	92
111-*rac*		^{t}Bu	H	H	60
112-*rac*			CH_3	H	61

* Synthesized from the titanium(IV) dichloride complex and 2.1 equiv Grignard reagent

2.1).[88] Treatment of a solution of the respective monochloride complex in THF at -35 °C with the appropriate organometallic alkylating reagent, followed by warming the reaction mixture to room temperature, gives the intensely colored paramagnetic π-allyl complexes **98-112** in moderate to high yields. For all titanocene templates, both the η^3-allyl and η^3-crotyl complexes are dark purple, while the corresponding cinnamyl complexes are dark blue.

The characterization of allylic complexes **98-112** was accomplished by infrared spectroscopy and either elemental or high resolution mass spectrometry. It is known that an infrared absorption band between 1480 and 1540 cm^{-1} of moderate to strong intensity is characteristic of the asymmetric C=C stretch for alkali and transition metals allylic anions.[115,116] This absorption band is strongly influenced by the substitution pattern of the ligand and the geometry of the substituents attached. For instance, the absorption bands for $Cp_2Ti(\eta^3\text{-}C_3H_{5\text{-}n}R_n)$ complexes are as follows: (allyl) = 1509 cm^{-1}; (2-methylallyl) = 1480 cm^{-1}; (1-methylallyl) = 1533 cm^{-1}; and (1,3-dimethylallyl) = 1546 cm^{-1}.[115] In addition, the frequency of the asymmetric C=C stretch of the allylic anions increases according to the sequence: 2-methylallyl < cyclohexenyl < *anti*-1-methylallyl < allyl < *syn*-1-methylallyl.[115] Accordingly, the infrared absorption bands of complexes **98-104** and the *meso*-stereoisomers of **105-110** clearly indicate that these complexes are η^3-coordinated and that all of the 1-substituted allyl complexes have the thermodynamically preferred *syn*-configuration (Table 2.2). However, the infrared spectra of the *rac*-stereoisomers are not as definitive: in some cases (complexes **105**, **107** and **111**), the spectra show absorption bands characteristic of η^3-coordination, but in other cases the absorption bands are located at higher frequency than expected (complex **106**) or more than one absorption band is seen in the region for the $C{=}C_{asymm}$ absorption (complex **112**). The infrared spectra of these latter complexes suggest that they may exist in more than one coordination mode (both η^3 and η^1-coordination) or may adopt either a distorted η^3-coordination or σ, π-coordination.[34,59] This IR data foreshadows marked differences in the reactivity observed for *rac* and *meso* isomers of these complexes.

Table 2.2. Infrared Absorptions for C=C$_{asymm}$ Band.



	Z	R	R'	R"	IR C=C $_{asymm}$(cm^{-1})
98	C	H	H	H	1506
99			H	CH_3	1489
100			CH_3	H	1531
101			Ph	H	1529
102	Si		H	H	1509
103			H	CH_3	1489
104			CH_3	H	-
105-*meso*	C	$SiMe_3$	H	H	1504
105-*rac*			H	H	1505
106-*meso*			CH_3	H	1549
106-*rac*			CH_3	H	1551
107-*meso*			Ph	H	1534
107-*rac*			Ph	H	1533
108-*meso*	Si	$SiMe_3$	H	H	1509
109-*meso*			CH_3	H	1534
110-*meso*	C	^{i}Pr	CH_3	H	1529, 1496
111-*rac*		^{t}Bu	H	H	1496
112-*rac*			CH_3	H	1552, 1535,1493

2.3.3. Radical Addition to *ansa*-Bridged Titanocene η^3–Allyl Complexes

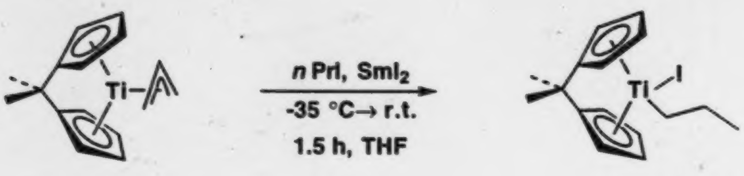
Central carbon alkylation of the *ansa*-[1]-titanocene allyl complexes **98-112** was investigated using various free radical generating protocols that were shown to be compatible with the highly reactive and air-sensitive Ti(III) complexes, **48** and **53**.[39,42] The predominant radical generating methodology used in this investigation was the alkyl halide/samarium(II) iodide protocol.[117,118] Other radical generation strategies investigated, in an attempt to extend the scope of some of the reactions, include samarocene[119] and bis[hydrotris(3,5-dimethylpyrazolyl)borato)]samarium(II)[120] in place of samarium(II) iodide, as well as photolytic decomposition of dialkyl mercury compounds[121] and titanocene-mediated epoxide-opening reaction.[45]

A. Reactions of *ansa*-[1]-Titanocene Allyl Complexes.

Since the ancillary ligands on these titanocene complexes induce a considerably strained geometry and cause a significant re-hybridization of the metallocene fragment,[64,65] alkylation of the unsubstituted ansa-[1]-titanocene allyl complexes was first investigated to determine whether these complexes retain the selectivity for central carbon alkylation.

Thus, treatment of the unsubstituted carbon bridged allyl complex **98** with one equivalent each of SmI_2 and an alkyl halide at -35 °C followed by warming to room temperature gave results dependent on the alkyl halide used. Surprisingly, iodo *n*-propyl complex **113** was formed upon treatment of complex **98** with one equivalent each of *n*-propyl iodide and SmI_2 in THF at low temperature (Equation 2.4). In a control experiment, no reaction was observed when a mixture of complex **98** and SmI_2 alone was stirred at room temperature for the same duration. The formation of complex **113** is best rationalized by the sequence of steps outlined in Scheme 2.16, commencing with abstraction of iodide by Ti(III) rather than by SmI_2 from the *n*-propyl iodide to give the Ti(IV) iodo allyl complex **114** and *n*-propyl radical. Complex **114** can then lose the allyl ligand with a concomitant reduction of titanium to give the trivalent titanium iodo complex **115**, which is then attacked by available *n*-propyl radicals to give complex **113**.

Alternatively, reduction of complex **114** by SmI_2 would regenerate starting material (complex **98**) which could react with *in situ* generated *n*-propyl radicals eventually leading to decomposition products. The reaction of complex **98** with *n*-propyl iodide and SmI_2 at room temperature is in contrast to the analogous reaction with $Cp^*_2Ti(\eta^3\text{-}C_3H_5)$ **48**, which requires much higher temperature,[39,42] suggesting the operation of a different mechanism in the present case.



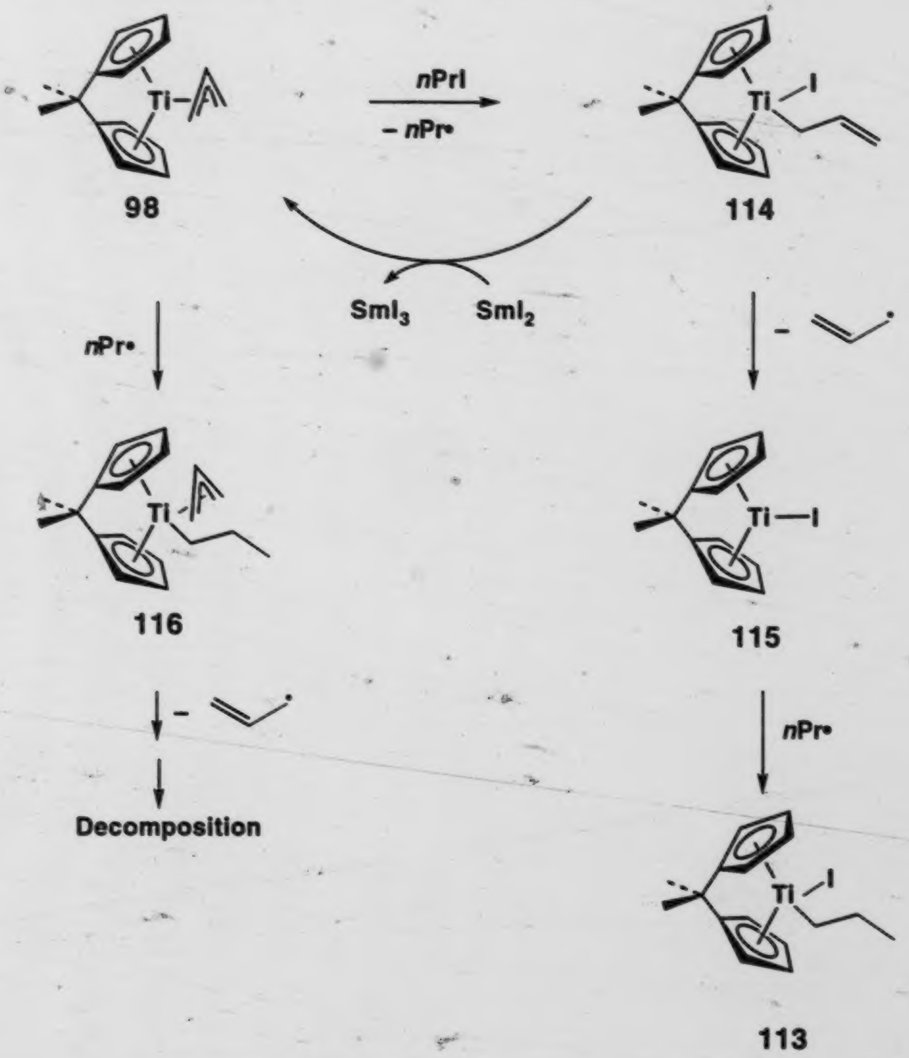
(2.4)

98 **113** (51%)

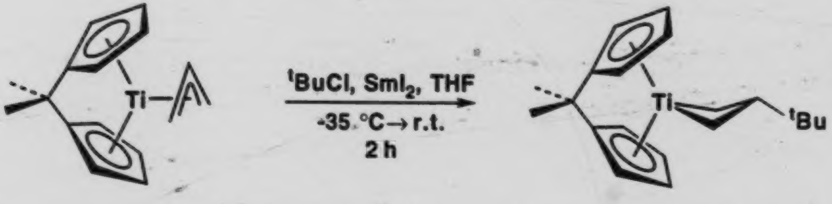
Complex **113** was identified on the basis of ^1H and ^{13}C spectroscopy. Resonances at δ 7.64 (dd, J = 5.4, 3.2 Hz), 6.73 (dd, 5.2, 3.2 Hz), 4.79 (dd, J = 4.8, 2.7 Hz) and 4.58 (dd, J = 5.0, 2.6 Hz) in the ^1H NMR spectrum are assigned to the methine protons of the cyclopentadienyl rings, while the singlets at δ 0.92 and 0.80, assigned to the methyl groups on the methano-bridge, indicate the expected lateral dissymmetry of this complex. The propyl substituent is indicated by a three-hydrogen triplet at δ 0.82 (J = 6.2 Hz) assigned to the methyl group, and two multiplets at δ 1.35 and 1.11 assigned to the methylene groups. The eleven carbon resonances in the ^{13}C NMR spectrum of complex **113** lend further support to the assigned structure. The four methine (125.3, 123.4, 109.6 and 109.2) and one quaternary (112.2) carbon resonances in the aromatic region of the spectrum, assigned to the carbon atoms of the two cyclopentadienyl rings, confirm the lateral dissymmetry of **113**. The resonances for the other carbon atoms of the ancillary ligand are observed at δ 22.3 and 19.7, assigned to the methyl groups, and at δ 35.5 for the quaternary carbon atom. The propyl substituent is clearly indicated by the signals at δ

87.6 (methylene α-carbon), 29.9 (β-methylene carbon), and 23.0 (terminal methyl group). An analytically pure sample of **113** was obtained by recrystallization from a cold (-35 °C) pentane solution.

Scheme 2.16


Ti
98
nPrI
- nPr•
Ti
I
114
SmI$_3$
SmI$_2$
nPr•
-
Ti
116
Ti
I
115
-
Decomposition
nPr•
Ti
I
113

In contrast to the product obtained from *n*-propyl iodide, β-*tert*-butyl titanacycle **117** was obtained in moderate yield when complex **98** was treated with 2-chloro-2-methylpropane and SmI_2 (Equation 2.5). Supporting the structural assignment of



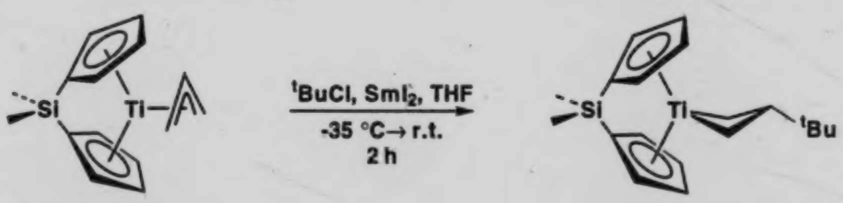
(2.5)

98 **117** (51%)

complex **117** is the ^1H NMR spectrum, which includes two apparent triplets at δ 2.73 (J = 10.0 Hz) and 2.32 (J = 10.0 Hz), assigned to the up and down sets of α-methylene protons, which show homonuclear correlation to the upfield signal at δ 0.06 (quintet, J = 10.0 Hz, 1H) characteristic of the β-methine proton.[1,2,25,41,42] The four narrow triplets at δ 5.99, 5.82, 5.23 and 5.13, all with J = 2.5 Hz, are assigned to the methine protons on the cyclopentadienyl rings and clearly indicate the top-to-bottom dissymmetry of complex **117**. In addition, the singlets observed at δ 1.22 (6H) and 1.03 (9H) ppm corresponding to the two equivalent methyl groups on the methano-bridge and the three methyl groups of the *tert*-butyl substituent, respectively, account for the other signals in the NMR spectrum. The ^{13}C NMR APT spectrum fully supports the ^1H NMR assignments with the characteristic signals for α- and β-carbon atoms observed at δ 73.7 and δ 29.3, respectively. An analytically pure, red-brown micro-crystalline material, obtained from a saturated pentane solution cooled to -35 °C, confirmed the identity of complex **117**.

Only paramagnetic product mixtures are obtained when isopropyl, allyl and benzyl halides are used as radical precursors. These mixtures, when treated with excess $PbCl_2$ in THF, give only the corresponding titanium(IV) dichloride complex, indicating that the products contain either the starting π-allyl complex **98** or the corresponding monochloride complex **92**. It is not clear why only the *tert*-butyl radical successfully alkylates complex **93**.

The silyl-bridged complex **99** shows similar reactivity to complex **98**. Among various haloalkanes investigated, only the β-*tert*-butyl titanacycle **118** was again obtained (Equation 2.6), indicating that the nature of the one-atom bridge has little effect on the efficiency or scope of this reaction. The titanium(IV) iodo propyl complex analogous to **113** was not observed upon treatment with *n*-propyl iodide and SmI_2, and addition of other alkyl radicals to complex **99** only gave paramagnetic product mixtures.



(2.6)

99

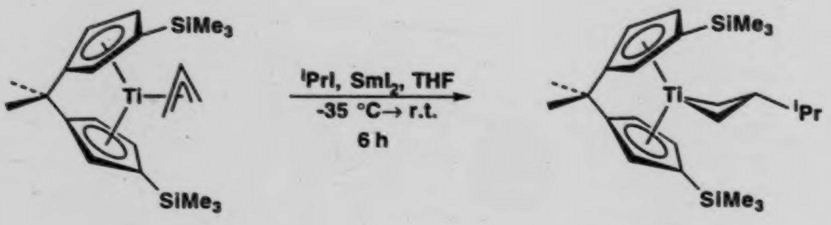
118 (38%)

The assignment of complex **118** is based on analysis of spectroscopic data completely analogous to complex **117**. The resonances that define the protons in the metallacyclic ring of complex **118** are very similar to those for complex **117**, indicating a close analogy in the structure of these two complexes. Corroboration of the ^1H NMR assignments is garnered from the ^{13}C NMR spectrum, which shows signals at δ 70.4 and δ 29.2 characteristic of the α- and β-carbon atoms of the titanacyclobutane ring. Significantly, there is an upfield shift of the signals for the two quaternary carbon atoms of the Cp rings and the equivalent methyl groups on the silyl-bridge due to the presence of the silicon atom.[111,112,122] Attempts to obtain an analytically pure sample of complex **118** failed, but high resolution mass spectrometry confirmed its elemental composition.

The limited radical alkylation reactivity observed for these complexes is analogous to that observed previously for the parent unbridged Cp system, $Cp_2Ti(\eta^3-C_3H_5)$ **48**.[39,42] These results indicate that the unsubstituted ancillary ligand is not sufficiently electron donating to facilitate effective orbital overlap between the singly occupied metal d-orbital and the π^*-orbital of the allyl ligand. Despite the limited scope, the milder reaction conditions required for alkylation with *tert*-butyl radical is in contrast to those required for alkylation of $Cp^*_2Ti(\eta^3-C_3H_5)$ **48** (Scheme 1.16), but very similar to those required for $(t\text{-}BuCp)_2Ti(\eta^3-C_3H_5)$ **53** (Scheme 1.17, Chapter 1.2).[39,42] This suggests that the mechanism for the central carbon alkylation of complexes **98** and **99** is similar to that proposed for complex **53** (*see* Scheme 1.17, Chapter 1.2), that is, samarium-mediated abstraction of the halide.

In order to probe the influence of increased electron density at the metal center on the scope of the radical alkylation reaction, allyl complexes with *ansa* bridged ligands bearing electron-donor substituents were investigated. The trimethylsilyl-substituted titanocene template was selected for this investigation primarily because of the ease of synthesizing the ligand system, as well as the straightforward synthesis and subsequent separation of the *rac* and *meso* diastereomeric titanocene(III) chloride complexes. Complexes with isopropyl- and *tert*-butyl-substituted titanocene template were also investigated and are discussed later. The diastereomer containing the *meso ansa*-[1]-bridged bis(1,1'-trimethylsilylcyclopentadienyl)titanium template (*e.g.* **105**) was first investigated because it was envisioned that more room was present in the wedge between the Cp rings to accommodate allyl ligand substituents by virtue of the *syn* orientation of the trimethylsilyl substituents. Complexes containing the *rac*-template were also investigated, with the results discussed in Section 2.3.3.F.

Thus, when the *meso* diastereomer of *ansa*-[1]-{dimethylmethano bis(3,3'-trimethylsilylcyclopentadienyl)}titanium η^3-allyl, **105-*meso***, is treated with 2-iodopropane and SmI_2 at low temperature, β-isopropyltitanacyclobutane complex **119a** is



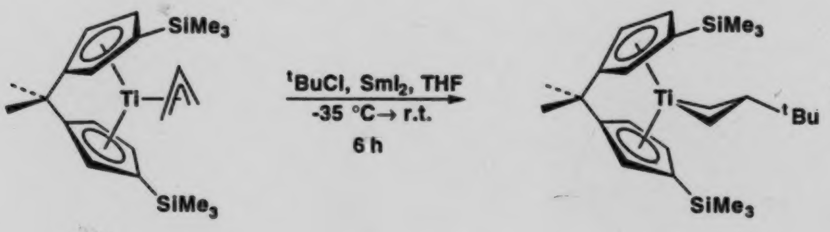
(2.7)

105-*meso* **119a** (78%)

formed cleanly and in high isolated yield (Equation 2.7). Structural assignment of complex **119a** follows from analysis of the spectroscopic data. The ^1H NMR spectrum shows signals for four inequivalent α-methylene hydrogen atoms at δ 2.79, 2.67, 2.12, 2.05, all appearing as triplets with 10.0 Hz coupling constant. The inequivalence of the α and α'-methylene hydrogen atoms is due to the *syn* arrangement of the trimethylsilyl groups (δ 0.25, 0.24 ppm) in the *meso ansa*-bridged system. This structural configuration is also reflected in the inequivalence of the methyl groups on the methano-bridge (singlets at δ 1.33 and 1.15 ppm) and the six methine hydrogen atoms on the cyclopentadienyl rings. The multiplet at δ 1.03 ppm and the two doublets at δ 1.16 (J = 6.4 Hz, 3H) and 1.15 (J = 6.0 Hz, 3H) ppm establish the presence of the isopropyl moiety. The gated-decoupled ^{13}C NMR spectrum also supports this structural assignment. The signals for the inequivalent α and α'-methylene carbons appear as triplets at δ 79.2 (J = 138.5 Hz), and 72.7 (J = 135.4 Hz), while that for the β-carbon appears as a doublet at δ 37.8 (J = 129.3 Hz). In addition to the signals for the cyclopentadienyl rings, resonances for methyl groups at δ 24.9 (q, J = 127.9 Hz) and 24.0 (q, J = 128.0 Hz), assigned to the isopropyl substituent, δ 23.2 (q, J = 125.4 Hz) and 22.6 (q, J = 125.4 Hz), assigned to the two inequivalent methyl groups of the methano-bridge, and δ -0.38 (q, J = 119.4 Hz) and

-0.71 (q, J = 118.9 Hz), assigned to the inequivalent trimethylsilyl groups also lend support to the proposed structure. The composition of complex **119a** is also supported by high resolution mass spectrometry of the air-sensitive, red-brown, micro-crystalline solid obtained by recrystallization from cold (-35 °C) pentane.

Treatment of complex **105-*meso*** with SmI_2 and 2-chloro-2-methylpropane, the precursor of the bulkier *tert*-butyl radical, also gives central carbon alkylation with comparable efficiency to the reaction of isopropyl radical (Equation 2.8). The spectroscopic data for compound **119b** are very similar to those for **119a**, showing



(2.8)

105-*meso*

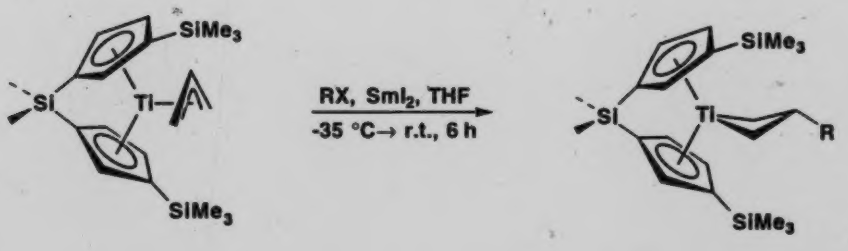
119b (81%)

characteristic ^1H and ^{13}C NMR signals for β-substituted titanacyclobutane. The expected triplets at δ 2.39, 2.15, 2.06 and 2.02 in the ^1H spectrum are readily assigned to the α and α'-methylene hydrogen atoms, and the upfield multiplet at δ 0.17 is assigned to the β-methine hydrogen atom. The nine-hydrogen singlet at δ 1.00 indicates the presence of the *tert*-butyl group, while the remaining signals in the spectrum are fully consistent with protons of the *meso* template. A ^1H-^1H homonuclear correlated spectrum confirmed the proton assignments for the hydrogen atoms in the metallacyclic ring. This structural assignment is also fully supported by a gated-decoupled ^{13}C NMR spectra, which shows the characteristic triplets at δ 72.1 (J = 139.4 Hz) and 65.5 (J = 134.6 Hz), assigned to the inequivalent α- and α'-methylene carbons, and doublet at δ 20.3 (J = 127.9 Hz), assigned to the β-methine carbon. In addition to the signals that define the *meso ansa*-bridged template, signals at δ 34.3 and 29.2 (q, J = 124.3 Hz) further support the presence of the *tert*-butyl group. A ^{13}C-^{1}H heteronuclear correlated spectrum enables the complete assignment of all hydrogen-bearing carbon atoms. The elemental composition of titanacyclobutane **119b** is confirmed by high resolution mass spectrometry.

The trimethylsilyl-substituted *ansa*-[1]-titanocene system, however, fails to support radical alkylation for other radical precursors, especially those that generate resonance stabilized radicals. Only intractable product mixtures are obtained, accompanied in some cases by the formation of the Ti(IV) dihalide complex. The limitations of this system, while not fully understood, will be discussed later.

The scope and reactivity of the silyl-bridged complex, **108-*meso***, towards central carbon alkylation are very similar to complex **105-*meso*** (Scheme 2.17). Central carbon alkylation is again limited to addition of the isopropyl and *tert*-butyl radicals, clearly indicating that the nature of the atom in the bridge linking the cyclopentadienyl rings has no significant effect on the alkylation reaction. The structural assignment of the resulting β-substituted titanacyclobutane complexes **120a** and **120b** follows from analysis of their spectroscopic data, which are very similar to those of complexes **119a** and **119b**. The

Scheme 2.17



108-*meso*

	R
120a	^{i}Pr (95%)
120b	^{t}Bu (80%)

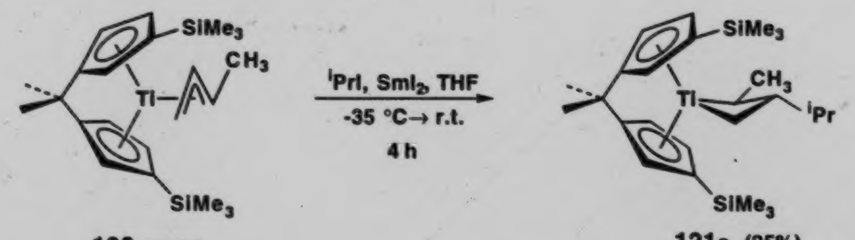
characteristic triplets (δ 2.77 (J = 10.0 Hz), 2.58 (J = 10.0 Hz), 2.22 (J = 10.0 Hz) and 2.09 (J = 10.0 Hz), assigned to the four inequivalent α-methylene hydrogen atoms, and the high field multiplet (δ - 0.24) assigned to the β-hydrogen are readily observed in the ^{1}H NMR spectrum of complex **120a**. The β-isopropyl substituent is indicated by the doublets at δ 1.13 (J = 6.3 Hz) and 1.10 (J = 6.3 Hz), and the multiplet at δ 0.88. The remaining signals in the spectrum are fully consistent with the *meso* silyl-bridged titanocene template. The ^{13}C NMR spectrum also fully supports the structure of complex **120a**, with characteristic signals observed for the α- and α'-methylene carbon atoms at δ 78.2 and 70.6 and the signal for the β-methine carbon atom at δ 13.6. The identity of complex **120a** is supported by high resolution mass spectrometry of the air-sensitive, red-brown crystalline solid obtained by recrystallization from cold (-35 °C) pentane.

The structural assignment of *t*-butylated complex **120b** is also based on close analogy to the carbon bridged analogue. The characteristic signals for the inequivalent α- and α'-methylene hydrogen atoms (δ 2.37, 2.13, 2.07 and 1.99), and the high field multiplet (δ 0.05) for the β-hydrogen atom are readily observed, while the singlet at δ 0.97 indicates the presence of the *tert*-butyl substituent. The gated decoupled ^{13}C spectrum further supports the assigned structure of **120b**, particularly the characteristic triplets at δ 70.5 and 63.6, for the α- and α'-methylene carbon atoms and the doublet at δ 18.1, for the β-methine carbon atom. High resolution mass spectrometry lends further support to the elemental composition.

B. Reactions of *ansa*-[1]-Titanocene Crotyl Complexes.

Having established that constraining the cyclopentadienyl rings with a one atom bridge does not prevent the central carbon alkylation reaction of the titanocene(III) η^3-allyl complexes, this investigation was then directed to the alkylation of substituted η^3-allyl complexes, the primary goal of this study. Using the unsubstituted *ansa*-bridged templates and both crotyl and 2-methylallyl ligands, the carbon-bridged (**99**, **100**) and the silicon-bridged (**103** and **104**) complexes (see p. 51, Table 2.1) were subjected to radical alkylation using 2-chloro-2-methylpropane. In contrast to simple allyl complexes **98** and **99**, however, no central carbon alkylation products were obtained. Only paramagnetic product mixtures are obtained when any of these crotyl complexes are treated with SmI_2 and any haloalkane.

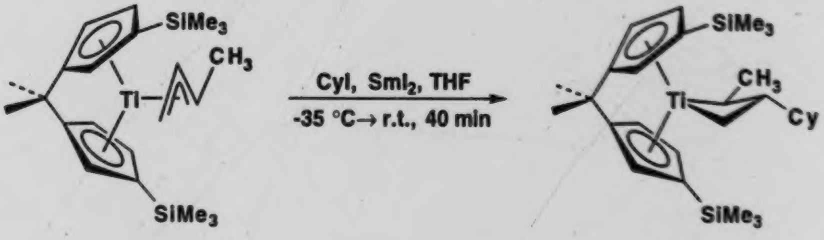
In contrast, the more electron-rich trimethylsilyl substituted *meso* templates, successfully undergo central carbon alkylation. Crotyl complex **106-*meso***, for example, gives 2,3-disubstituted titanacylobutane complexes **121a-c** when treated with non-stabilized organic radicals. Thus, treatment of complex **106-*meso*** with one equivalent each of SmI_2 and 2-iodopropane at low temperature results in the efficient synthesis of the red-brown 3-isopropyl-2-methyl titanacyclobutane complex **121a** (Equation 2.9), isolated in nearly quantitative yield.



106-*meso* **121a** (95%) (2.9)

Structural assignment of complex **121a** is based on the analysis of the spectroscopic data and the reasonable assumption that the stereochemistry of the starting crotyl complex is *syn* based on the asymmetric absorption IR band at 1533 cm^{-1} for 1-methylallyl complexes. The ^1H NMR spectrum of complex **121a** shows one-hydrogen resonances at δ 2.40 (t, J = 10.0 Hz) and 2.14 (t, J = 10.0 Hz) which are assigned to the two inequivalent α-methylene protons, while a signal at δ 2.65 (dq, J = 10.0, 6.9 Hz) is assigned to the α-methine proton. The characteristic high field signal of the β-hydrogen is observed as a multiplet at δ -0.27 and the doublet at δ 1.65 (J = 6.9 Hz) is assigned to the methyl group at the α-position. Doublets at δ 1.12 (J = 6.7 Hz) and 0.83 (J = 6.7 Hz) and the multiplet at δ 1.80 are assigned to the diastereotopic methyl groups of the isopropyl moiety. The characteristic resonances for the inequivalent trimethylsilyl groups are located in the upfield region of the spectrum as singlets at δ 0.24 and -0.27. The other signals in the spectrum are characteristic of the protons of the ancillary ligand (*vide supra*). The gated-decoupled ^{13}C NMR fully supports this structural assignment for complex **121a**. A doublet at δ 89.5 (J = 132.0 Hz) and triplet at δ 66.6 (J = 134.9) are readily assigned to the α-methine and α-methylene carbons, respectively, consistent with other titanacyclobutane complexes and the expected deshielding effects of the additional methyl substituent. The eight signals between 18 and 30 ppm are due to the methine and methyl carbon atoms of the isopropyl group, the carbon atom of the methyl group on the α-carbon, the β-methine carbon atom and the carbon atoms of the two methyl groups on the methano-bridge. Because of extensive overlap of these signals and without additional correlated spectroscopy, however, complete assignment is not possible. The remaining signals in the spectrum are characteristic of the ancillary ligand of these complexes. An analytically pure sample of **121a**, obtained from a cold (-35 °C) pentane solution, confirmed the identity of this complex.

The addition of cyclohexyl radical to crotyl complex **106-*meso***, using cyclohexyl iodide as the radical precursor, also proceeds efficiently to the central carbon position of the crotyl ligand, giving the 3-cyclohexyl-2-methyl titanacyclobutane complex **121b** in nearly quantitative yield (Equation 2.10). A comparison of the ^{1}H spectrum of complex **121b** with that of **121a** showed analogous signals for the ancillary ligand and the titanacyclobutane moiety. In addition, signals for the cyclohexyl substituent are observed as multiplets at δ 1.77 (4H), 1.31 (6H) and 0.99 (1H) for the methylene and methine

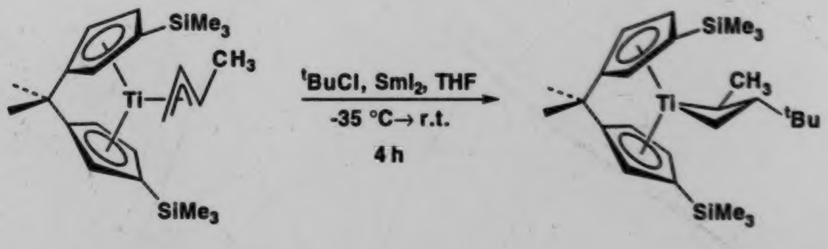

SiMe₃
CH₃
Ti
SiMe₃
CyI, SmI₂, THF
-35 °C→ r.t., 40 min
SiMe₃
CH₃
Ti
Cy
SiMe₃

(2.10)

106-*meso* **121b (97%)**

hydrogen atoms. Further support for the structure of complex **121b** is garnered from the gated-decoupled ^{13}C NMR spectrum. The doublets at δ 89.2 (J = 127.4 Hz) and 22.6 (J = 130.0 Hz) are assigned to the α- and β- methine carbons of the four-membered heterocycle, respectively, while the triplet at δ 69.6 (J = 135.4 Hz) is assigned to the remaining α-methylene carbon in the ring. In addition to the characteristic signals for the ancillary ligand, the remaining six signals in the spectrum at δ 43.2 (d, J = 125.6 Hz), 35.0 (t, J = 122.1 Hz), 30.5 (t, J = 128.8 Hz), 28.0 (t, J = 124.0 Hz), 27.6 (t, J = 122.1 Hz) and 27.5 (t, J = 122.1 Hz) are assigned to the methine and methylene carbon atoms of the cyclohexyl moiety. A high resolution mass spectral analysis of a pure sample of complex **121b** further supports its elemental composition.

The bulky *tert*-butyl radical is also trapped by complex **106-*meso*** with similarly high efficiency, giving 3-*tert*-butyl-2-methyl titanacyclobutane complex **121c** (Equation 2.11). The ^{1}H NMR spectrum of complex **121c** shows the characteristic signals for the


SiMe₃
CH₃
Ti
SiMe₃
ᵗBuCl, SmI₂, THF
-35 °C→ r.t.
4 h
SiMe₃
CH₃
Ti
ᵗBu
SiMe₃

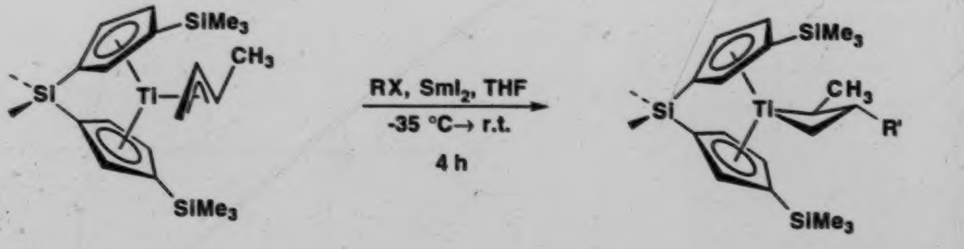
(2.11)

106-*meso* **121c (81%)**

four-membered metallacycle at δ 2.30 (t, J = 10.0 Hz) and 2.21 (t, J = 10.0 Hz) for the α-methylene hydrogen atoms, in addition to multiplets at δ 2.49 and -0.03 for the α-methine and β-methine hydrogen atoms. The doublet at δ 1.65 (J = 6.8 Hz, 3H), assigned to the α-methyl group, and 9-hydrogen singlet at δ 1.01, assigned to the *tert*-butyl group are fully consistent with the structure of **121c**. Further spectroscopic analysis was not possible due to the lower thermal stability of this complex compared to complexes **121a** and **121b**.

The reactivity of the analogous silicon-bridged crotyl complex, **109-*meso***, towards organic radicals generated using the alkyl halide/SmI_2 strategy is similar to that observed for complex **106-*meso***, giving 2,3-disubstituted titanacyclobutane complexes **122a** and **122b** on addition of the isopropyl and *tert*-butyl radicals, respectively (Scheme 2.18). One significant problem with alkylation using this template, however, is that the resulting titanacyclobutane complexes are typically contaminated by paramagnetic impurities, which appear to promote the thermal decomposition of the titanacyclobutane compounds. In the cases of complexes **122a** and **122b**, complete spectroscopic assignments were not possible due to this thermal instability and the difficulty in separating the paramagnetic

Scheme 2.18



109-*meso*

	R
122a	^{i}Pr (65%)
122b	^{t}Bu (trace)

impurities. The ^{1}H NMR spectrum of complex **122a**, however, clearly indicates the presence of the 2,3-disubstituted metallacycle: characteristic triplets at δ 2.45 (J = 10.0 Hz), 2.31 (J = 10.0 Hz), assigned to the two inequivalent α-methylene hydrogen atoms, and multiplets at δ 2.76 and - 0.31, assigned to the α- and β-methine hydrogen atoms, respectively, clearly define the four-membered ring. Resonances consistent with the ancillary ligand and the isopropyl group are also observed.

As observed with allyl complexes **105-*meso*** and **108-*meso*** (*vide supra*), stabilized radicals failed to give central carbon alkylation products with complex **106-*meso*** in reactions mediated by SmI_2.

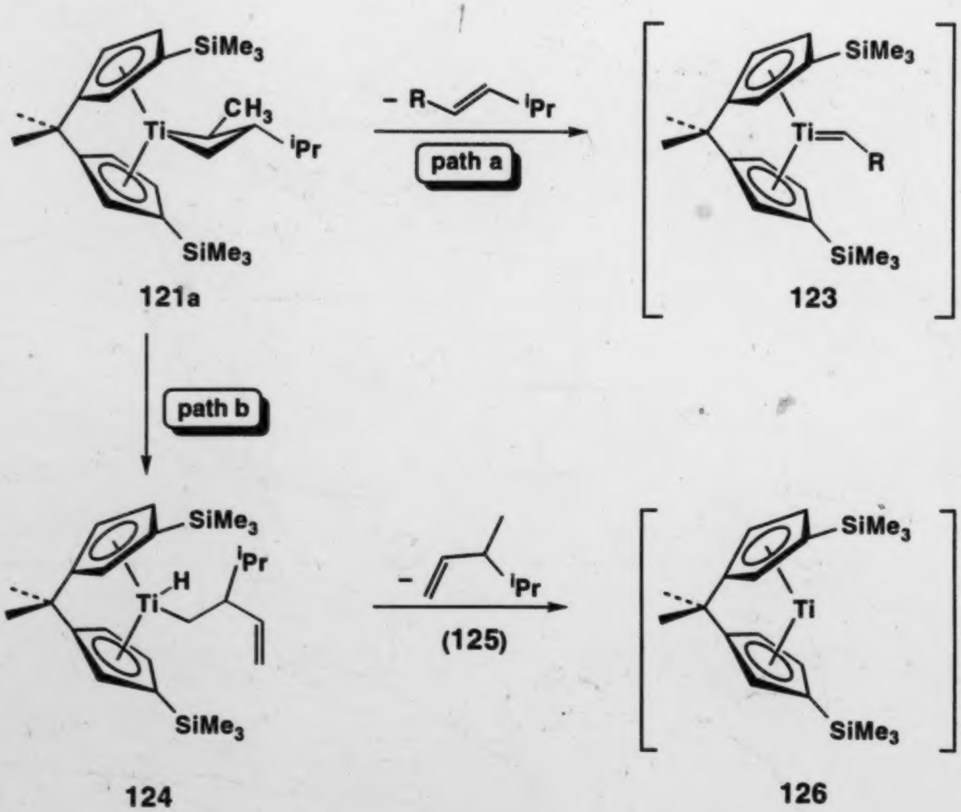
Significantly, the synthesis of these 2,3-disubstituted titanacyclobutane complexes via the SmI_2/alkyl halide methodology represents the first free radical alkylation of the central carbon of substituted allyl complexes. It appears that the larger space in the wedge between the Cp rings, coupled with a reasonable donor character in the ancillary ligand, indeed promotes alkylation at the central carbon position of the crotyl moiety, perhaps by facilitating η^3-coordination of the crotyl ligand, in keeping with our original postulate.

None of the 2,3-disubstituted titanacyclobutane complexes derived from the crotyl ligand are indefinitely stable in solution at room temperature. They are considerably more persistent at low temperature (< -35 °C), especially when stored in the solid state. There are two logical pathways by which this decomposition can occur (Scheme 2.19): a) cycloreversion to give one of two possible regio-isomeric titanium alkylidene compounds (path a), or b) β-hydride elimination from the α-methyl position, followed by reductive elimination, to give 3,4-dimethylpentene and an unstable Ti(II) species (path b). To determine the origin of this instability, the 3-isopropyl-2-methyl titanacyclobutane

121a was allowed to decompose in the presence of excess diphenylacetylene, a known trapping agent for 'low-valent' titanium. If the decomposition occurs via path (a), 2,3-diphenyltitanacyclobutene products are expected, while a Ti(II)-diphenylacetylene adduct is expected if the decomposition proceeds via path (b). In the event, analysis of the product mixture shows the presence of 3,4-dimethyl-1-pentene **125** and tetraphenyltitanacyclopentadiene **127** (Scheme 2.20), indicating that decomposition appears to proceed by β-hydride elimination at the α-methyl position.

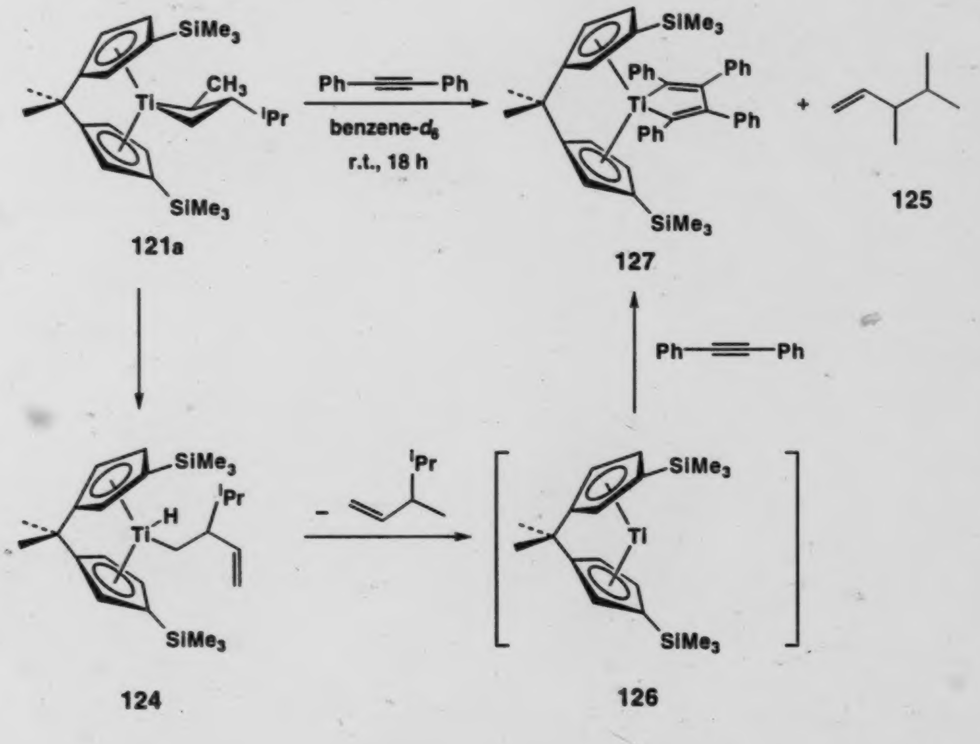
After separation of the volatile organic product, the identity of complex **127** was assigned by spectroscopic analysis. The intact ancillary ligand template is revealed by

Scheme 2.19

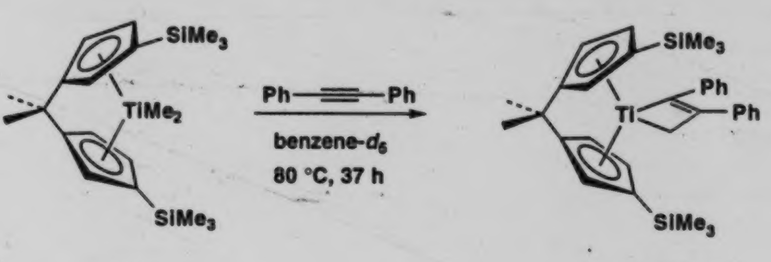

SiMe3
CH3
Ti
iPr
SiMe3
121a
- R iPr
path a
Ti
R
SiMe3
SiMe3
123
path b
SiMe3
iPr
H
Ti
SiMe3
124
- iPr
(125)
SiMe3
Ti
SiMe3
126

the three triplets at δ 7.73, 5.45 and 4.60 and, in addition, a singlet at δ 0.09 for both TMS groups defines the top-to-bottom symmetry consistent with complex **127**. The inequivalence of the two methyl groups on the methano-bridge (δ 1.59 and 1.49) indicates the expected lateral dissymmetry, which is supported by the four ^{13}C NMR resonances at δ 206.3, 192.8, 150.6 and 147.1 for the quaternary carbon atoms of the titanacyclopentadiene ring. The other NMR resonances are fully consistent with the assigned structure and high resolution mass spectrometry confirms the elemental composition of complex **127**. ^{1}H NMR spectroscopy and GCMS analyses of 3,4-dimethyl-1-pentene **125** was used to confirm its identity.

Scheme 2.20


SiMe₃
CH₃
Ti
ⁱPr
SiMe₃
121a
Ph—≡—Ph
benzene-d₆
r.t., 18 h
SiMe₃
Ph
Ph
Ti
Ph
Ph
SiMe₃
127
+
125
Ph—≡—Ph
SiMe₃
ⁱPr
H
Ti
SiMe₃
124
ⁱPr
−
SiMe₃
Ti
SiMe₃
126

In order to prove that no titanium alkylidene species is formed during the decomposition of the α-methyl titanacyclobutane complexes, the 2,3-diphenyl titanacyclobutene complex **129**, one of the expected diphenylacetylene-trapping products from sigma-bond metathesis of titanacyclobutane complexes, was prepared independently



128 **129** (70%)

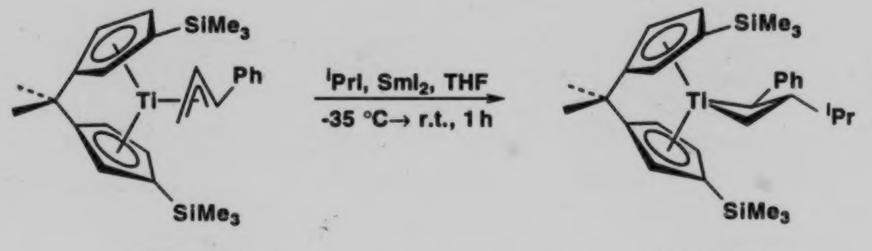
(2.12)

by a well-established procedure.[55-57,123] Thus, a benzene-d_6 solution of the dimethyl complex **128** and diphenylacetylene was heated at 80 °C for 37 hours in a sealed NMR tube to give complex **129** in good yield (Equation 2.12). Analysis of the spectral data of complex **129** clearly indicates that it is not formed during the decomposition of titanacyclobutane complex **121a**. Key spectroscopic features are a two-hydrogen singlet at δ 3.79 in the ^{1}H NMR and the concomitant ^{13}C NMR resonance appearing as a triplet at δ 71.7 for the α-methylene group. In addition, the ^{13}C NMR signals for the α- and β-quaternary carbon atoms are observed as singlets at δ 217.7 and 149.2, respectively, similar to the previously reported 2,3-diphenyl bis(cyclopentadienyl)titanacyclobutene complex.[57,123] The other resonances in the NMR spectra of complex **129** are fully consistent with the assigned structure.

C. Reactions of *ansa*-[1]-Titanocene Cinnamyl Complex.

To investigate further the scope of the radical trapping reaction of substituted-allyl complexes, the alkylation of the cinnamyl complex **107-*meso*** was investigated. As for the crotyl complexes, the complex with the unsubstituted *ansa*-bridged template was first investigated. Thus, treatment of the cinnamyl complex **101** with one equivalent each of an alkyl halide and SmI_2 at -35 °C gave complex product mixtures. The ^{1}H NMR spectra of the crude reaction mixtures showed the presence of small amounts of the expected titanacycles for isopropyl, *tert*-butyl and cyclohexyl radical, however, the major components were paramagnetic, precluding identification and separation. The low yield of putative titanacyclobutane products observed here is greater than that seen using the crotyl complexes, perhaps indicating a small "aryl" effect, analogous to that defined for palladium allyl additions.[11]

More encouraging results were obtained when the 1,1'-bis(trimethylsilyl)-substituted titanocene cinnamyl complex **107-*meso*** was subjected to radical alkylation. Complex **107-*meso***, when treated with one equivalent each of 2-iodopropane and samarium (II) iodide at low temperature, gave 3-isopropyl-2-phenyl titanacyclobutane complex **130a** in good isolated yield, unaccompanied by significant paramagnetic impurities (Equation 2.13). Spectroscopic features typical for 2,3-disubstituted titanacyclobutane complexes are exemplified by the spectroscopy of complex **130a**. The



(2.13)

107-*meso*

130a (73%)

^{1}H NMR resonances that define the hydrocarbon moiety of the titanacycle appear as triplets at δ 2.61 (J = 10.0 Hz) and 2.48 (J = 10.0 Hz) for the α-methylene hydrogen atoms, a multiplet at δ 1.55 for the β-methine hydrogen, and a downfield doublet at δ 4.02 (J = 12.0 Hz) for the α-methine hydrogen (Table 2.3). The signals for both the α- and β-methine hydrogen atoms are shifted downfield by 2.20 and 1.82 ppm, respectively, compared to crotyl alkylation products **121a-c**, presumably a consequence of the electron withdrawing character and anisotropic deshielding effect of the α-phenyl group. The presence of the isopropyl moiety is indicated by the two diastereotopic methyl doublets at δ 1.04 (J = 6.6 Hz) and 0.94 (J = 6.6 Hz), and the complex multiplet at δ 0.85. As is the case for other 2,3-disubstituted titanacyclobutane complexes discussed previously, the top-to-bottom dissymmetry is clearly indicated by the six doublet of doublets between δ 7.0 and 4.3 ppm assigned to the methine hydrogen atoms of the cyclopentadienyl rings, as well as the upfield singlets at δ 0.27 and 0.25 assigned to the non-equivalent TMS groups. The ^{13}C NMR spectrum fully supports the assigned structure, particularly the resonances at δ 92.2 (d, J = 134.7 Hz), 70.0 (t, 134.3 Hz) and 23.7 (d, J = 152.8 Hz), assigned to the two α-carbon atoms and the β-carbon atom, respectively. The deshielding of the ^{13}C resonance for the α-methylene carbon is again attributed to the electron withdrawing effect of the phenyl substituent. High resolution mass spectral analysis of a purified sample of **130a** (hexanes, -35 °C) confirms its elemental composition.

Similarly, when complex **107-*meso*** was treated with either the bulky *tert*-butyl or cyclohexyl radicals, the corresponding titanacyclobutane complexes **130b** and **130c** are obtained in very good yields (Scheme 2.21). The structural assignments of these complexes were determined in a manner similar to complex **130a** and selected ^{1}H NMR spectroscopic data are shown in Table 2.3. It is instructive to note the similarity in the chemical shifts and coupling constants for protons in complexes **130a-c** (Table 2.3), clearly suggesting a close structural similarity among these complexes.

Scheme 2.21

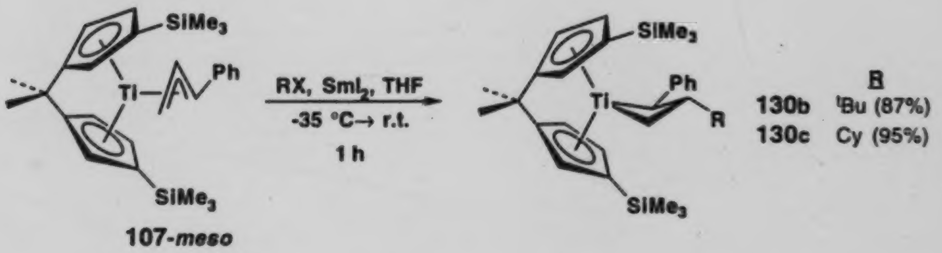


Table 2.3. Selected ^{1}H NMR Resonances for Titanacyclobutane Complexes **130a** - **130c**

	R = ^{i}Pr, **130a** δ (m, J, I)*	R = ^{t}Bu, **130b** δ (m, J, I)*	R = Cy, **130c** δ (m, J, I)*
Ti-CH_2	2.61 (t, 10, 1H); 2.48 (t, 10, 1H)	2.63 (t, 10, 1H); 2.48 (t, 10, 1H)	2.75 (t, 10, 1H); 2.55 (t, 10, 1H)
Ti-C$\underline{H}$(Ph)	4.02 (d, 12, 1H)	3.99 (d, 12, 1H)	4.08 (d, 12, 1H)
β-CH	0.85 (m, 1H)	1.05 (m, 1H)	0.85 (m, 1H)
$C(CH_3)_2$	1.29 (s, 3H); 1.03 (s, 3H)	1.28 (s, 3H); 0.94 (s, 3H)	1.30 (s, 3H); 1.04 (s, 3H)
TMS	0.27 (s, 9H); 0.25 (s, 9H)	0.26 (s, 18H)	0.27 (s, 9H); 0.26 (s, 9H)

* δ = chemical shift, m = multiplicity, J = J_{HH} in Hz, and I = integral.

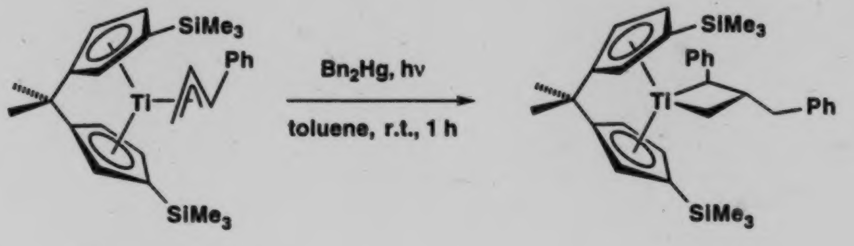
Other alkyl halides, precursors to more stabilized organic radicals, failed to give central carbon alkylation using SmI_2-mediated methodology. This observation indicates that there is no particular advantage, either in scope or reactivity, to the use of cinnamyl complexes compared with either the allyl or crotyl systems.

D. Reactions with Stabilized Radicals.

As indicated previously, the most significant limitation to alkylation of the *ansa*-bridged substituted allyl complexes is that no titanacyclobutane complexes are obtained when treated with stabilized radicals (*e.g.*, allyl and benzyl) generated using the SmI_2/alkyl halide strategy. All attempts to make this process proceed to titanacyclobutane generally resulted only in the production of the corresponding Ti(IV) dihalide complex, the dimerization or disproportionation products derived from the organic free radical, and considerable amounts of unidentifiable decomposition material.

As a consequence, several alternative radical generating protocols were briefly investigated. The use of the more strongly reducing samarocene (Cp_2Sm)[124] and bis[hydrotris(3,5-dimethylpyrazolyl)borato]samarium(II) ($Sm(HBpz^*{}_3)_2$)[120] in place of SmI_2 as the reductant also fail to give metallacyclobutane products, producing product mixtures similar to those obtained from SmI_2. Moving away from samarium-based reagents, the use of Ti(III)-mediated epoxide-opening[45] to generate the β-oxy-alkyl radicals also led only to dark red-brown, intractable product mixtures in all cases. It is mystifying as to the reason for the failure of stabilized radicals to alkylate these η^3-allyl complexes, however, it is possible that with these methods, the rate of radical generation is simply too fast for effective scavenging by Ti(III), resulting in a high concentration of organic free radical intermediates that then access non-productive reaction pathways. It is also possible that, these resonance-stabilized radicals may not be energetic enough to add to the less electron-rich *ansa*-bridged systems compared to the decamethyltitanocene system, possibly resulting in very low rate of radical addition to the η^3-allyl complexes.

Successful central carbon alkylation with stabilized radicals was finally accomplished by using photolytic decomposition of dialkylmercury compounds. Thus, the photolysis of cinnamyl complex **107-*meso*** and dibenzylmercury in toluene using a 450W high pressure mercury lamp efficiently gives the corresponding 3-benzyl-2-phenyl titanacyclobutane **130d**, isolated in high yield (Equation 2.14).



(2.14)

107-*meso*

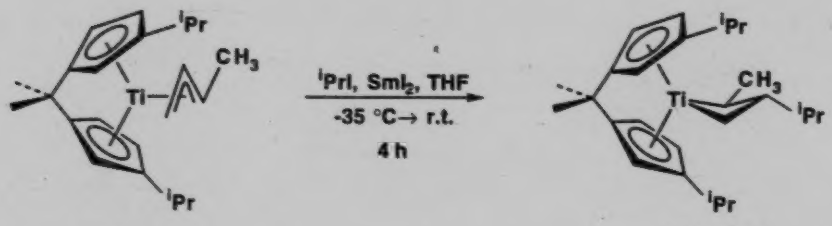
130d (80%)

The structure of complex **130d** rests on the analysis of spectroscopic data, which show patterns consistent with previous titanacycles in this series. The ^1H NMR resonances that define the four-membered metallacyclic ring are observed at δ 3.23 and 1.91 (t, J = 10.0 Hz) assigned to the α-methylene hydrogen atoms, δ 3.95 (d, J = 12.0 Hz) assigned to the α-methine hydrogen atom and δ 1.21 (complex multiplet) assigned to the β-methine hydrogen atom. The typical signals denoting the ancillary ligand are also readily observed. Six multiplets between 7.32 and 6.85 ppm clearly indicate the presence of two phenyl groups, and the second-order two-hydrogen multiplet at δ 2.44, assigned to the benzylic methylene, confirms the presence of the benzyl substituent. The ^{13}C NMR spectrum further supports the structure of **130d**, especially the resonances at δ 93.7 (d, J = 135.8 Hz), 72.6 (t, J = 134.4 Hz) and 16.1 (d, J = 131 Hz), characteristic of the α-carbon atoms and the β-carbon atom of the titanacyclobutane, respectively. The additional singlet at δ 142.1 is assigned to the *ipso*-carbon of the benzyl substituent and the benzyl methylene triplet at δ 43.1 (J = 127.8 Hz) confirms the presence of the benzyl substituent. High resolution mass spectrometry confirms the elemental composition of this complex.

Presumably, photolytic decomposition of dialkylmercury compounds produces alkyl radicals at a much slower rate than the other radical generating methods, allowing the complex to trap the radicals to give the metallacyclobutane complex rather than engage in bimolecular organic reactions. This reactivity is promising but impractical, primarily due to the acute toxicity of organic mercury compounds. As a consequence, new radical generating methods are the subject of continuing research in the Stryker group.

E. Other *ansa*-[1]-Titanocene Templates.

To assess the minimum electron density required to facilitate central carbon alkylation of substituted η^3-allyl complexes, we looked at *ansa*-[1]-titanocene templates with other substituents. Isopropyl substituents on the *ansa*-[1]-titanocene template also facilitate central carbon alkylation of substituted η^3-allyl complexes, as illustrated by the reaction of crotyl complex **110-*meso*** with isopropyl radical. Thus, treating complex **110-*meso*** with SmI_2 and 2-iodopropane at low temperature affords the corresponding 2,3-disubstituted titanacyclobutane complex **131** in moderate yield (Equation 2.15). Consistent with the behavior of α-methyl titanacyclobutane complexes **121** and **122**, this



(2.15)

110-*meso*

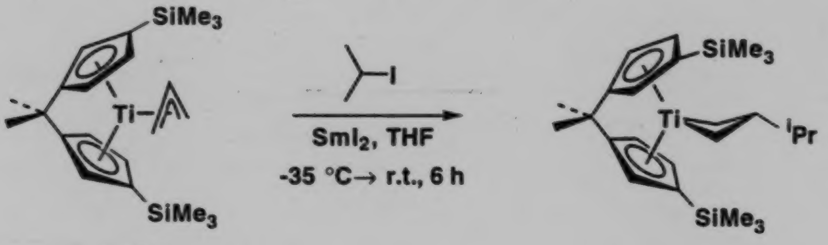
131 (55%)

complex also decomposes slowly in solution, yielding the expected decomposition products (see Scheme 2.17 above). The ^1H NMR spectrum of complex **131** nonetheless confirms its identity, showing resonances at δ 2.28 (t, J = 10.0 Hz) and 1.80 (dd, J = 10.0 Hz) assigned to the two inequivalent α-methylene proton, and a signal at δ 2.75 (dq, J = 12.0, 6.0 Hz), which overlaps with the signal for one of the ancillary ligand isopropyl methine protons, assigned to the α-methine proton of the titanacyclobutane ring. In addition, a characteristic high field signal for the β-hydrogen is observed as a multiplet at δ -0.38. The other signals in the ^1H NMR spectrum, as well as the ^{13}C APT NMR spectrum, are fully consistent with the assigned structure of complex **131**.

An extensive investigation of the reactivity of substituted allyl complexes with this isopropyl-substituted *ansa*-[1]-titanocene template was not undertaken, but the above result is consistent with an electron density argument for facilitating radical coupling.

F. Reactions of *rac* Diastereomers.

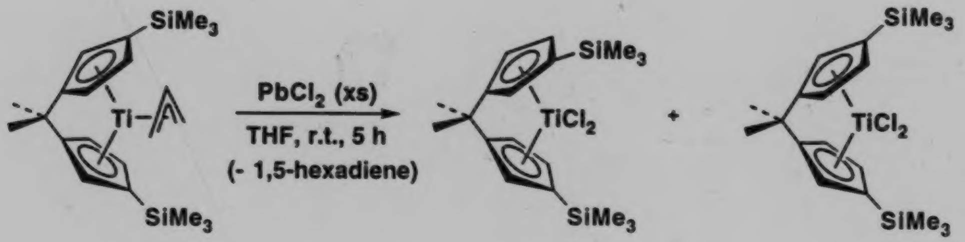
In order to determine what effect the spatial orientation of the cyclopentadienyl substituents has on the radical alkylation reaction, an investigation of the analogous '*rac*'-*ansa*-[1]-bridged trimethylsilyl-substituted titanocene allyl, crotyl and cinnamyl complexes **105-*rac***, **106-*rac***, **107-*rac***, respectively, as well as the *ansa*-[1]-bridged *tert*-butyl-substituted titanocene allyl and crotyl complexes **111-*rac*** and **112-*rac***, was also conducted. The trimethylsilyl-substituted titanocene η^3-allyl complex **105-*rac*** showed a very surprising and unprecedented reactivity pattern upon addition of the isopropyl radical (Equation. 2.16). Complex **105-*rac*** undergoes central carbon alkylation cleanly, but with concomitant isomerization to give the *meso* titanacyclobutane product **119a** exclusively and in very high yield! This unique reaction is specific to the isopropyl radical; no other organic radicals investigated to date induce this template isomerization reactivity.



105-*rac* **119a (80%) !** (2.16)

The *rac* to *meso* isomerization of complex **105-*rac*** is observed not only during this one alkylation reaction, but also in the oxidation of the '*rac*' allyl complex using $PbCl_2$ under heterogeneous conditions (Scheme 2.22).[125] Furthermore, this reaction proceeds with an astonishing dependence on the stirring rate of the reaction mixture. Thus, oxidation of the *rac* allyl complex **105-*rac*** using a suspension of $PbCl_2$ in THF, *without agitation of the reaction mixture*, leads to a 3 : 1 isomeric ratio of the *meso* and *rac* dichlorides **132-*meso*** and **132-*rac***, respectively. The isomerization reaction occurs to a much lesser extent (1 : 2 *meso* to *rac*) when the oxidation mixture is rapidly stirred. At this time, we do not have any reasonable explanation to account for this observation. It is important to note that $PbCl_2$ oxidation of allyl complex **105-*meso***, or crotyl complex

Scheme 2.22



[rac] meso rac

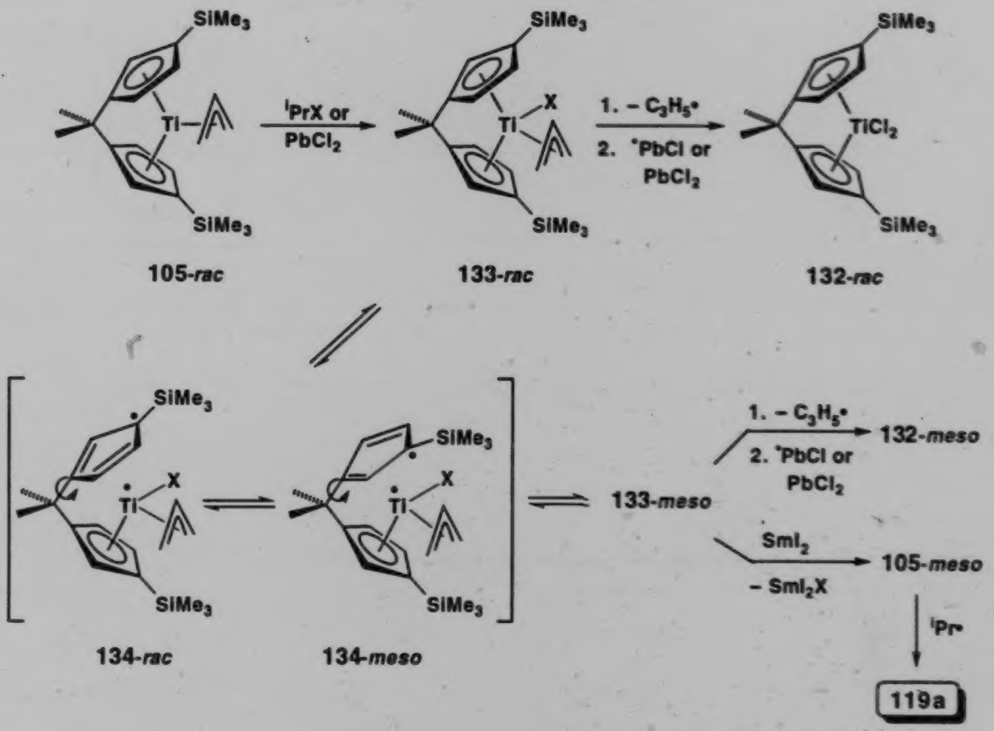
105-*rac* **132-*meso*** **132-*rac***

• no stirring	3	:	1	(quant.)
• rapid stirring	1	:	2	

106-*meso* does not lead to any observable isomerization to the *rac* diastereomer. In addition, no isomerization is observed during $PbCl_2$ oxidation of allyl complex **106-*rac***, or during $PbCl_2$ oxidation of either titanocene monochloride complexes **94-*meso*** or **94-*rac*** to the corresponding dichlorides **132-*meso*** and **132-*rac***.

The observation of template isomerization in both the alkylation and oxidation suggests that a common intermediate may be involved in the skeletal isomerization of complex **105-*rac***. Both rearrangements are perhaps best understood according to the postulated sequence of reactions shown in Scheme 2.23. The most logical reaction is halide abstraction by allyl complex **105-*rac*** from either $PbCl_2$ or the alkyl halide to give titanium(IV) allyl halide complex **133-*rac***. This titanium(IV) intermediate can either lose the allyl ligand by homolytic cleavage, giving the titanium(III) halide complex, or

Scheme 2.23


SiMe3
Ti
SiMe3
105-rac
iPrX or
PbCl2
SiMe3
X
Ti
SiMe3
133-rac
1. – C3H5•
2. •PbCl or
PbCl2
SiMe3
TiCl2
SiMe3
132-rac
SiMe3
X
Ti
SiMe3
134-rac
SiMe3
X
Ti
SiMe3
134-meso
133-meso
1. – C3H5•
2. •PbCl or
PbCl2
132-meso
SmI2
– SmI2X
105-meso
iPr•
119a

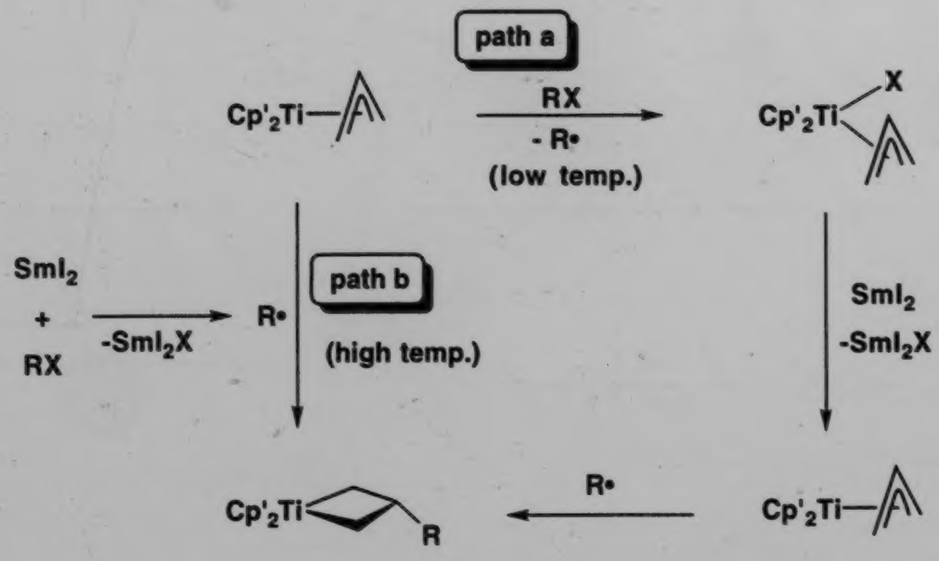
undergo the observed skeletal rearrangement (Scheme 2.23). In the former case, the resulting Ti(III) complex can abstract a second halide from the lead dichloride or monochloride to give the unrearranged complex, **132-*rac***. For the skeletal rearrangement, we postulate an initial homolytic cleavage of the Ti-Cp bond, giving the Ti(III) species **134-*rac***, that rearranges to the thermodynamically preferred complex **134-*meso*** by rotation of the disassociated Cp ring. Re-coordination of the Cp ligand gives the rearranged Ti(IV) intermediate **133-*meso***, which then suffers the same fate as complex **133-*rac*** to give the corresponding Ti(IV) dichloride **132-*meso***. For the SmI_2 reaction, Ti(IV) intermediate **133-*meso*** can be reduced by SmI_2 to give allyl complex **105-*meso***, which is then alkylated by an isopropyl radical to afford titanacyclobutane **119a**.

Similar diastereomeric rearrangements of *rac/meso* mixtures of *ansa*-metallocene complexes under photochemical activation, have been recently reported and postulated to proceed via species analogous to those proposed here.[126-129] Another such diastereomeric rearrangement was recently observed in which a *rac/meso* mixture of ethylenebis(indenyl)zirconium bis(dialkylamine) complexes could be converted thermally to a mixture enriched in the *rac* diastereomer. This isomerization is also suggested to involve de-coordination–rotation–re-coordination of one arm of the ligand.[130-133]

G. Postulated Mechanism for Radical Addition.

In order to arrive at a reasonable mechanistic rationalization for the radical alkylation of allyl titanium complexes, it is instructive to summarize the various reaction conditions required for these reactions. A previous study from this group determined that SmI_2-mediated central carbon alkylation of the sterically shielded 17-electron $Cp^*_2Ti(\eta^3\text{-}C_3H_5)$ **48** proceeds at -35 °C for stabilized radical precursors, but requires 45 °C for non-stabilized radical precursors.[39,42] In contrast, however, analogous reactions of the sterically less congested $({}^tBu\text{-}Cp)_2Ti(\eta^3\text{-}C_3H_5)$ **53** proceed at -35 °C for both stabilized and non-stabilized radical precursors.[39,42] The alkylation reactions of the significantly less congested *ansa*-bridged η^3-allyl complexes with non-stabilized radical precursors also occur at -35 °C, suggesting a similarity in the reaction mechanisms. Since it is also known that SmI_2 reacts with unactivated alkyl halides only at reflux in THF, while activated alkyl halides react at room temperature,[117,118] we propose two mechanistic rationalizations to account for the dependence of the reaction conditions on the nature of the radical precursors (Scheme 2.24). The low temperature alkylation of sterically more accessible allyl complexes using unactivated alkyl halides must be initiated by a reaction between the allyl complex and the alkyl halide to generate an unstable Ti(IV) allyl halide complex, along with an alkyl radical (Scheme 2.24, path a). The former complex is reduced by SmI_2 to regenerate the Ti(III) allyl complex, which then reacts with the organic radical to yield the titanacyclobutane complex.

Scheme 2.24



Cp' = $C_5(CH_3)_5$, ${}^tBu\text{-}C_5H_4$ or *ansa*-bridged system

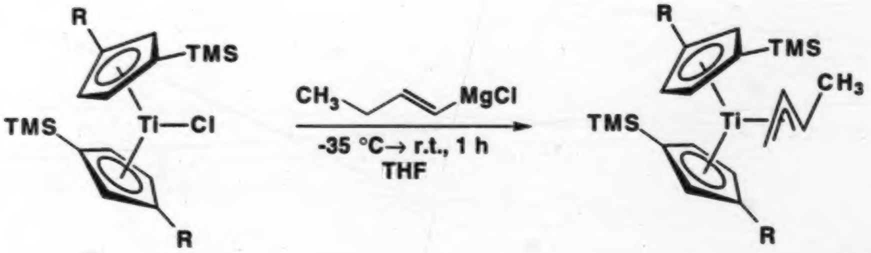
In contrast, the reaction of alkyl halide with the sterically more congested $Cp^*_2Ti(\eta^3\text{-}C_3H_5)$ **48**, in which close approach of the alkyl halide to the metal is significantly inhibited, is most likely initiated by SmI_2-mediated halide abstraction generating the corresponding alkyl radical, which subsequently reacts with the allyl complex (Scheme 2.24, path b). For the reactions of allyl complexes with allylic and benzylic halides, only the SmI_2-initiated pathway is likely to be operative, while in the sterically more accessible *tert*-butyl and *ansa*-bridged complexes, both mechanisms may operate competitively. In the latter case, rapid generation of the stabilized radicals by both reaction pathways is expected to result in a high concentration of organic radical, as well as both Sm(III) species and the unstable Ti(IV) allyl halide complex. If the addition of stabilized radicals to the Ti(III) allyl complex is slow, radical disproportionation and dimerization reactions become important.

Circumstantial evidence to support the mechanism proposed in path (a) is provided by the isomerization reactions discussed in the preceding section (Scheme 2.20). The mechanistic rationalization for the skeletal rearrangement of allyl complex **105-*rac*** requires formation of the Ti(IV) allyl halide intermediate **133-meso**, which can be reduced back to the starting Ti(III) allyl complex by SmI_2. This is the most plausible explanation for the reaction that gives titanacyclobutane complex **119a** from allyl complex **105-*rac***. Additional support for this mechanism is garnered from the reaction of unsubstituted *ansa*-[1]-titanocene allyl complex **98** with *n*-propyl iodide and SmI_2, which yields the Ti(IV) propyl iodo complex **113**, presumably formed by a similar initial step (Scheme 2.16, above). On this basis, therefore, it is reasonable to propose that the normal course of the alkylation reaction proceeds according to path (a) in Scheme 2.24.

H. Reactions of Non-*ansa*-Bridged Models.

Based on previous observations that a minimum level of electron density at the metal center is required to promote radical alkylation of substituted titanocene allyl complexes, control experiments using bis(1,3-disubstituted-cyclopentadienyl)titanium crotyl complexes **137** and **138** were performed to determine whether the cumulative electronic effects of these substituents alone can provide this minimum electronic requirement. The crotyl complexes **137** and **138** are readily prepared from the corresponding Ti(III) chloride complexes[134] by treatment with crotylmagnesium chloride at low temperature (Scheme 2.25). Treatment of either complex **137** or **138** with one equivalent each of 2-iodopropane and SmI_2 at low temperature, however, leads only to the corresponding Ti(III) iodo complexes **139** and **140** (Scheme 2.26). This reactivity suggests that the steric accessibility of the titanium center is at least similar to complex **53**

Scheme 2.25

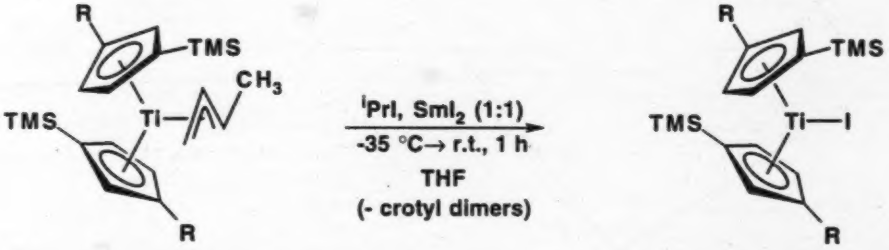

R
TMS
TMS
Ti—Cl
R
CH3
MgCl
-35 °C→ r.t., 1 h
THF
R
TMS
CH3
TMS
Ti
R

135 R = TMS
136 R = ^{t}Bu (2 diastereomers)

137 R = TMS (89 %)
138 R = ^{t}Bu (97 %)

($[^{t\text{-}Bu}Cp]_2Ti[\eta^3\text{-}C_3H_5]$), but that the loss of the crotyl ligand from the resulting Ti(IV) iodo crotyl intermediate is much faster than reduction by SmI_2. The most probable reason for this is that the metal center in the Ti(IV) iodo crotyl intermediate is relatively more crowded, rapidly ejecting the crotyl ligand to give the observed products (Scheme 2.26).

Scheme 2.26


R
TMS
CH3
TMS
Ti
R
^{i}PrI, SmI$_2$ (1:1)
-35 °C→ r.t., 1 h
THF
(- crotyl dimers)
R
TMS
TMS
Ti—I
R

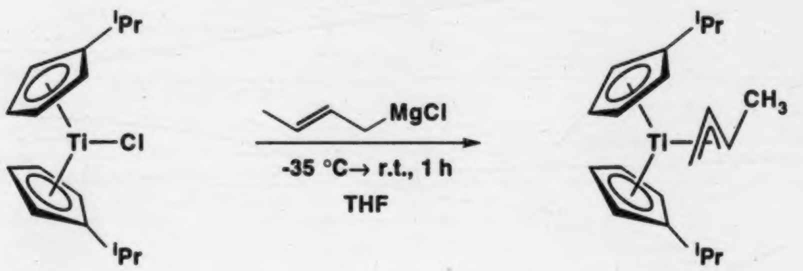
137 R = TMS
138 R = ^{t}Bu (2 diastereomers)

139 R = TMS (60%)
140 R = ^{t}Bu (60%)

Recently, Coville presented results addressing the relative orientation in space of alkyl substituents on the cyclopentadienyl rings of titanocene complexes.[135] For large groups, *e.g.*, TMS and *tert*-butyl groups, the substituents preferentially adopt an *anti*-

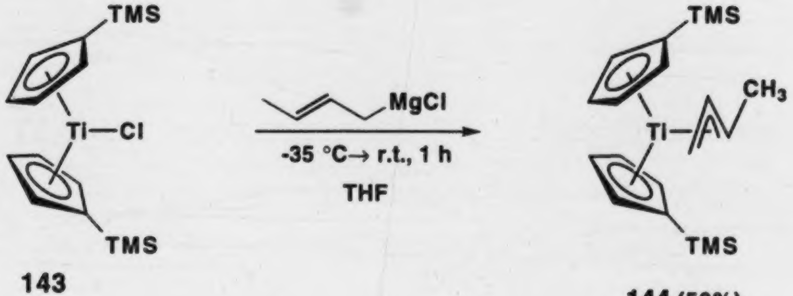
conformation (*i.e.*, the substituent on one Cp-ring is pointing in the opposite direction to the substituent on the other ring), but for smaller groups such as isopropyl, the substituents prefer a *syn*-conformation (*i.e.*, the substituents are eclipsed). As a consequence, we speculated that bis(isopropylcyclopentadienyl)titanium substituted allyl complexes may be amenable to central carbon alkylation reactions, since the *syn*-arrangement of the substituents corresponds to the *meso* orientation of the substituted *ansa*-[1]-titanocene templates which do support central carbon alkylation.

Consequently, bis(1,1'-isopropylcyclopentadienyl)titanium crotyl **142** was prepared by treatment of bis(isopropylcyclopentadienyl)titanium chloride **141** (prepared by treating $TiCl_3 \cdot 3THF$ with two equivalents of the lithium salt of isopropylcyclopentadiene) with one equivalent of crotylmagnesium chloride in THF at low temperature (Equation 2.17).



141 **142** (21%) (2.17)

Treatment of this complex with one equivalent each of 2-iodopropane and SmI_2 at low temperature failed to give titanacyclobutane formation, giving instead a paramagnetic product mixture. Oxidation of the crude mixture with $PbCl_2$ gave only the known bis(isopropylcyclopentadienyl)titanium dichloride complex.[135] The bis(trimethylsilylcyclopentadienyl)titanium crotyl complex **144**, prepared from the corresponding Ti(III) monochloride **143**[136] in a similar manner to complex **142**, was also investigated, despite the indication from Coville that the TMS groups would adopt the *anti*-conformation. As observed for crotyl complex **142**, only paramagnetic material was obtained when bis(trimethylsilylcyclopentadienyl)titanium crotyl **144** was treated with isopropyl radical (Equation 2.18). This reactivity is also similar to the reactivity of $Cp^*_2Ti(\eta\text{-}C_3H_4R)$ (R = Me, Ph), $(t\text{-}BuCp)_2Ti(\eta\text{-}C_3H_4R)$ (R = Me, Ph) and $Cp^*CpTi(\eta\text{-}C_3H_4R)$ (R = Me, Ph) previously reported.[58] These results suggest that the solution structure of these complexes presumably favors η^1-coordination of the crotyl ligand, preventing central carbon alkylation of the substituted allyl ligand.



143

144 (50%)

(2.18)

2.3.4. Radical Addition to Dialkylaminocyclopentadienyl Titanium η^3-Crotyl and η^3-Cinnamyl Complexes

In the previous section we presented results establishing that substituted η^3-allyl complexes of the *ansa*-[1]-titanocene template with sufficient space in the wedge between the cyclopentadienyl rings will undergo central carbon alkylation. This investigation also revealed that a minimum level of electron density is required to promote radical addition to the central carbon position of crotyl and cinnamyl complexes. To further probe this electronic requirement for radical addition, Ti(III) crotyl and cinnamyl complexes with cyclopentadienyl ligands substituted with strong donor substituents were investigated to determine whether greatly increased electron density alone is sufficient to promote regioselective alkylation. Titanocene complexes with amine and alkoxide atoms directly bonded to the cyclopentadienyl rings were considered the most viable candidates for this study.[66-77]

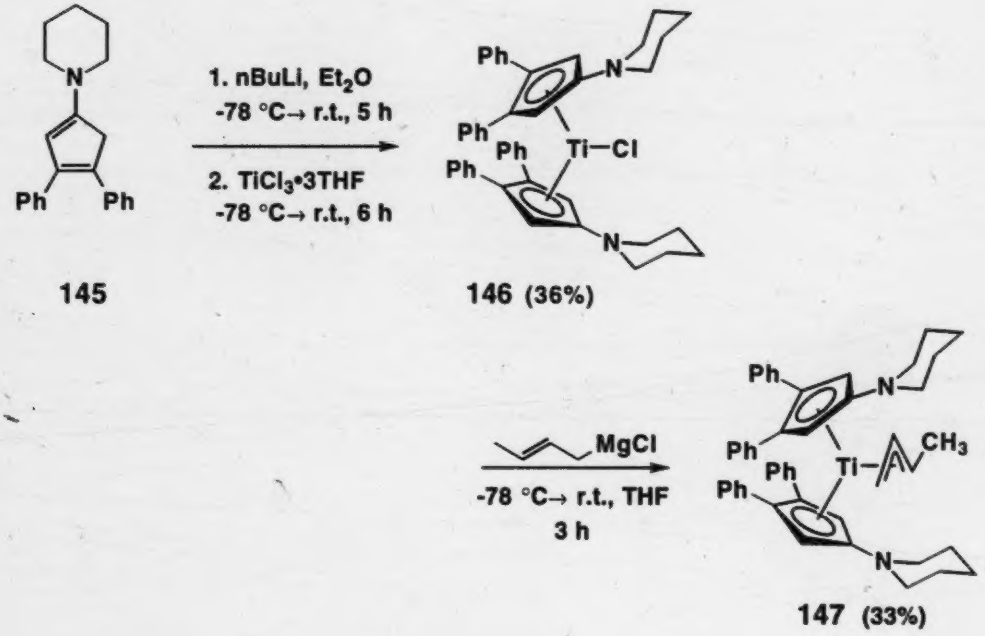
A. Synthesis of Crotyl and Cinnamyl Complexes.

The previously reported dimethylamino cyclopentadiene[71,74,75] ligand was considered ideal for this study, particularly because of the small steric profile of the dimethylamino group. However, due to difficulties associated with the preparation of this ligand, more robust but somewhat bulkier ligands were utilized instead.[68,137]

Based on availability, 3,4-diphenyl-1-piperidinocyclopentadienyl **145**[68] and 2-piperidinoindenyl **148**[137] were selected for initial investigation. These compounds were readily prepared by treating a mixture of piperidine and the corresponding ketone with catalytic amount of trifluoromethanesulfonic acid and heating to reflux in benzene. Synthesis of the aminotitanocene η^3-allyl complexes required for this study was accomplished by the sequence of reactions shown in Schemes 2.27 and 2.28. Addition of the lithium salt of **145** (2 equivalents), prepared by metallation using butyllithium, to $TiCl_3$•3THF in THF at -78 °C yields the dark brown bis(2-piperidino-3,4-diphenyl)titanium chloride **146** (Scheme 2.27). The corresponding crotyl complex was obtained by treating the monochloride complex with one equivalent of 1-methylallylmagnesium chloride in THF at -35 °C, which produces crotyl complex **147** as a brown amorphous solid (Scheme 2.27). These reactions are not very efficient, but provided sufficient material to proceed with the investigation. Characterization of these paramagnetic complexes was accomplished by infrared spectroscopy and, in the case of the monochloride complexes, $PbCl_2$ oxidation to the corresponding dichloride complexes was also used. Both elemental analysis and high resolution mass spectrometry failed for the paramagnetic complexes.

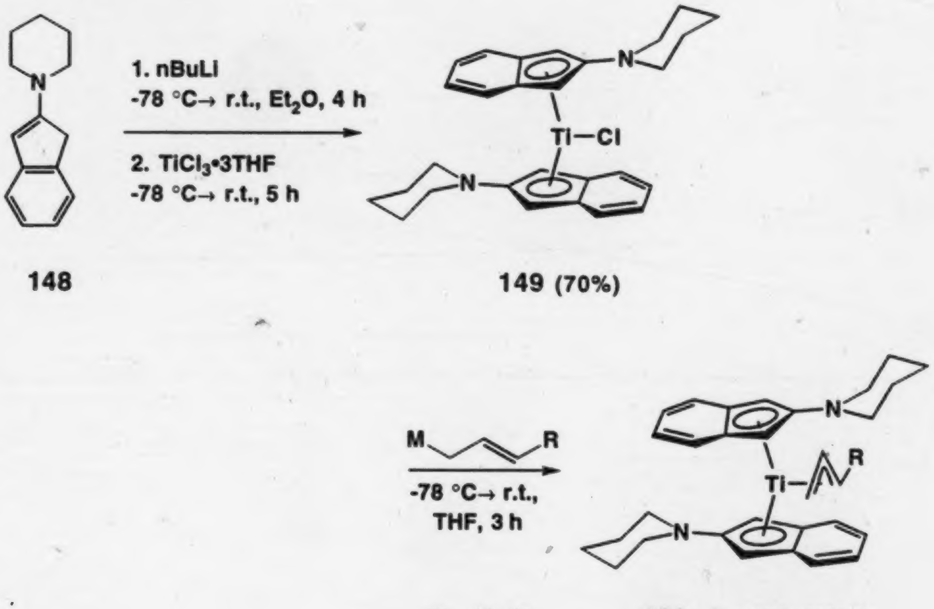
The corresponding crotyl and cinnamyl bis(2-piperidinoindenyl)titanium complexes **150** and **151** were obtained in a similar manner to crotyl complex **147** (Scheme 2.28). Treatment of the preformed lithium salt of **148**[138,139] (2 equivalents) with $TiCl_3$•3THF yields the dark brown bis(2-piperidinoindenyl)titanium chloride **149** in good yield (Scheme 2.28). The crotyl and cinnamyl complexes **150** and **151** were readily prepared in moderate yield by treatment of the monochloride complex **149** with the appropriate alkylating organometallic reagent. Crotyl complex **150** was obtained as an amorphous brown solid, while the cinnamyl complex **151** was obtained as a dark green crystalline solid. These paramagnetic titanium(III) complexes were characterized by infrared spectroscopy and elemental analyses. In the case of cinnamyl complex **151**, a X-ray crystallographic analysis was also obtained (see Experimental Section).

Scheme 2.27


N
Ph
Ph
145
1. nBuLi, Et₂O
-78 °C→ r.t., 5 h
2. TiCl₃•3THF
-78 °C→ r.t., 6 h
Ph
Ph
Ph
Ph
N
N
Ti—Cl
146 (36%)
MgCl
-78 °C→ r.t., THF
3 h
Ph
Ph
Ph
Ph
N
N
Ti
CH₃
147 (33%)

The single-crystal X-ray analysis of cinnamyl complex **151** reveals some interesting structural features. The cinnamyl ligand is unsymmetrically coordinated to the titanium center with a very short Ti-C(1) bond [2.318(6)Å] and successively longer Ti-C(2) [2.351(6)Å] and Ti-C(3) [2.448(6)Å] bond distances. In fact, the Ti-C(1) and Ti-C(2) bond distances are among the shortest known for Group IV metallocene allyl complexes, which typically range from 2.54 Å to 2.272 Å.[60,140-146] The longer Ti-C(3) bond, compared to the Ti-C(1) bond length, typical of complexes in which titanium binds to a

Scheme 2.28



148

149 (70%)

M = MgCl

M = Li

150 R = CH$_3$ (45%)

151 R = Ph (51%)

substituted carbon atom, may be due to repulsive interactions between the phenyl ring and the indenyl ligand. A particularly interesting structural feature of complex **151** is that the atoms of the *syn*-phenyl substituent lie in the same plane as the three-carbon allylic moiety (Figure 2.1), strongly suggesting a continuous resonance interaction of the π-systems of the phenyl ring and the three-carbon allylic moiety. The shortened C(3)-C(4) single bond distance [1.480(8)Å] clearly indicates double bond character in this bond, supporting the suggestion of extended π-conjugation in the cinnamyl ligand. The conjugated π-system of the cinnamyl moiety may account for the *green* color of this complex contrasting to the brown crotyl complexes **147** and **150**, which do not engage in

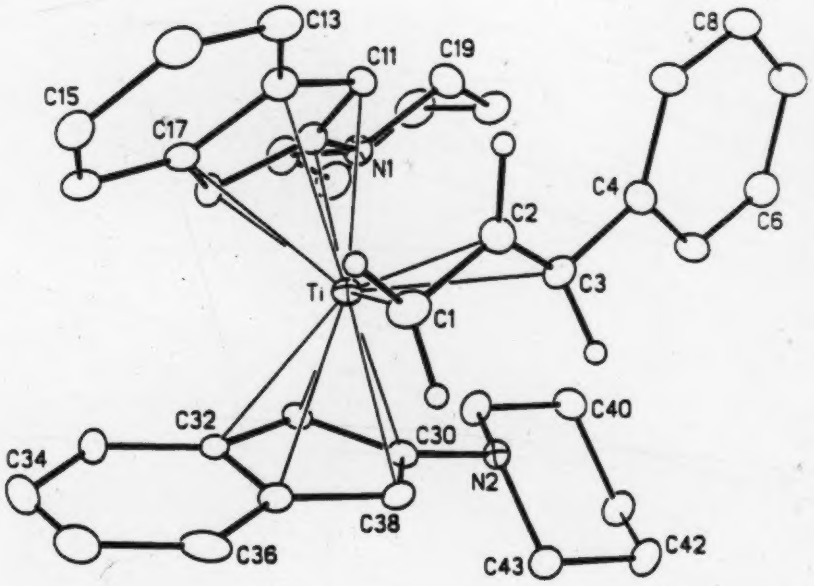


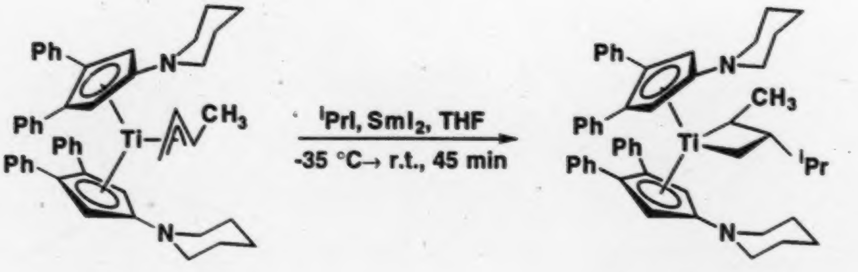
Figure 2.1. Perspective view of the bis(η^5-2-piperidinoindenyl)(η^3-1-phenylallyl)Ti(III) **151** showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The only hydrogen atoms shown are those of the titanium-coordinated carbon atoms of the phenylallyl group (with arbitrarily small thermal parameters).

such a resonance interaction. The differences in color between the *purple ansa*-bridged allyl and crotyl complexes and the *dark blue* cinnamyl complexes (*vide supra*) may also reflect a *syn*, co-planar phenyl ring in those cinnamyl complexes. As reported previously for other aminometallocene complexes,[66,69] the carbon-nitrogen single bond distances of complex **151** (C(10)-N(1) = 1.416(7)Å and C(30)-N(2) = 1.409(7)Å) are shorter than the typical carbon-nitrogen single bond, consistent with a strong mesomeric interaction of the nitrogen lone pair with the indenyl ring. The short titanium-carbon bond distances may reflect greater π-back bonding from the titanium center to the cinnamyl ligand as a consequence of the greater donor character of the amino-substituted indenyl ligands.

B. Radical Addition to Crotyl and Cinnamyl Complexes.

1. Bis(2-piperidino-3,4-diphenylcyclopentadienyl)titanium Crotyl Complex.

Radical addition to the piperidinotitanocene crotyl and cinnamyl complexes proceeded with very remarkable results. Unlike previously investigated unbridged titanocene substituted allyl complexes, these compounds are very good traps for organic radicals, affording 2,3-disubstituted titanacyclobutane complexes in the process. Thus, treating a cold (-35 °C) THF solution containing one equivalent each of crotyl complex **147** and SmI_2 with one equivalent 2-iodopropane gave the central carbon alkylation product **152a** as a red-brown solid in moderate isolated yield (Equation 2.19). Characterization of titanacyclobutane **152a** rests on analysis of the ^1H NMR spectrum and comparisons to spectra of similar 2,3-disubstituted titanacyclobutane complexes. The ^1H NMR spectrum of **152a** showed resonances typical for the four-membered heterocyclic ring at δ 2.70 (t, J = 10.0 Hz) and 2.39 (t, J = 10.0 Hz), assigned to the two inequivalent α-methylene hydrogen atoms, a multiplet at 2.61 assigned to the α-methine proton, and the characteristic upfield multiplet at δ - 0.10, assigned to the β-methine

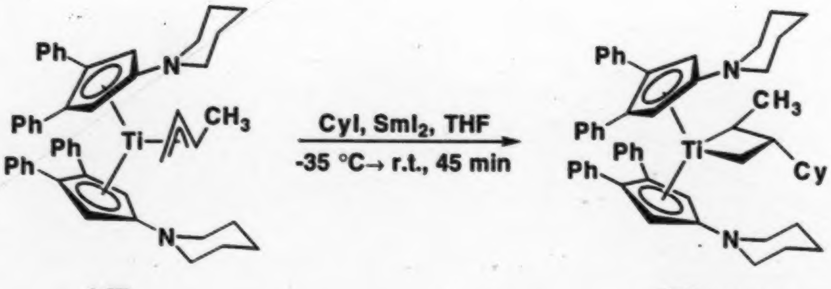


(2.19)

147 **152a (55%)**

hydrogen atom. The resonance for the α-methyl group is observed as a doublet at δ 1.67 (J = 6.8 Hz), while the resonances for the diastereotopic isopropyl methyl groups are observed as doublets at δ 1.06 and 1.00. The four one-hydrogen doublets at δ 6.01 (J = 2.8 Hz), 5.53 (J = 3.0 Hz), 5.36 (J = 2.8 Hz) and 4.58 (J = 2.7 Hz) assigned to the methine hydrogen atoms of the cyclopentadienyl rings clearly illustrate the top-to-bottom and side-to-side dissymmetry of complex **152a**. The remaining signals in the spectrum are assigned to the phenyl methine hydrogen atoms (multiplets between δ 7.61 and 6.89) and the piperidino methylene hydrogen atoms (broad multiplets at δ 2.81, 2.61, 2.39, 1.43, 1.27 and 1.23). Further characterization of this extremely air-sensitive complex was not possible due to its slow decomposition in solution.

Crotyl complex **147** also successfully traps cyclohexyl radicals to afford the corresponding titanacyclobutane complex. Treating a cold (-35 °C) THF solution containing one equivalent each of complex **147** and SmI_2 with one equivalent cyclohexyl iodide gave 3-cyclohexyl-2-methyl titanacyclobutane **152b** in moderate isolated yield (Equation 2.20). Similar to the β-isopropyl titanacyclobutane **152a**, the thermal instability of complex **152b** precludes comprehensive spectral analysis. The ^1H NMR spectrum of **152b**, however, shows the key resonances pertaining to the four-membered heterocyclic ring: δ 2.86 (t, J = 10.0 Hz) and 2.38 (t, J = 10.0 Hz) for the α-methylene hydrogen atoms, 2.72 (multiplet) for the α-methine proton, and -0.24 for the β-methine

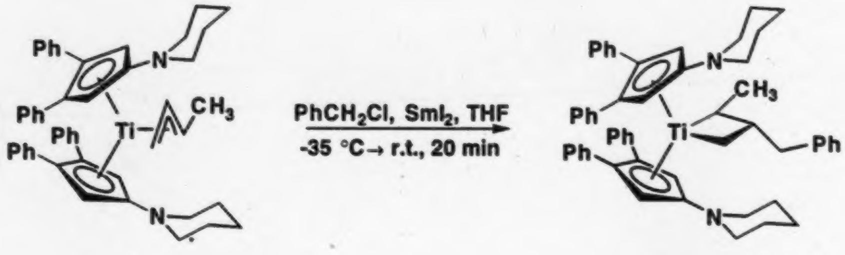

Ph
N
Ph
Ph
Ti
CH3
Ph
N
Cyl, SmI2, THF
-35 °C→ r.t., 45 min
Ph
N
CH3
Ph
Ph
Ti
Ph
Cy
N

147 **152b (67%)**

(2.20)

hydrogen atom. The resonances for the substituents on the titanacyclobutane ring are observed at δ 1.70 (d, J = 6.8 Hz) for the α-methyl group, and 2.72, 1.96, 1.81, 1.63, 1.05, 0.95 (multiplets) for the β-cyclohexyl substituent. The remaining resonances in the spectrum are consistent with the ancillary ligands.

Quite remarkably, crotyl complex **147** traps benzyl radical to afford the corresponding titanacyclobutane complex, though with low efficiency (Equation 2.21). The low yield of complex **152c** coupled with its thermal instability, as previously observed for complexes **152a** and **152b**, prevented complete characterization of this


Ph
N
Ph
Ph
Ti
CH3
Ph
N
PhCH2Cl, SmI2, THF
-35 °C→ r.t., 20 min
Ph
N
CH3
Ph
Ph
Ti
Ph
Ph
N

147 **152c (20%)**

(2.21)

complex. However, some of the characteristic ^{1}H NMR signals indicating the identity of this complex are observed: triplets at δ 2.47 (J = 10.0 Hz) and 2.27 (J = 10.0 Hz) assigned to the α-methylene hydrogen atoms, an upfield multiplet at δ 0.01 assigned to the β-hydrogen atom, and the three-hydrogen doublet at 1.78 (J = 6.8 Hz) assigned to the

α-methyl group. The other signals in the spectrum are consistent with both the ancillary ligands and a benzyl substituent. This is the first successful alkylation of a substituted allyl complex with benzyl radicals by using SmI_2 methodology.

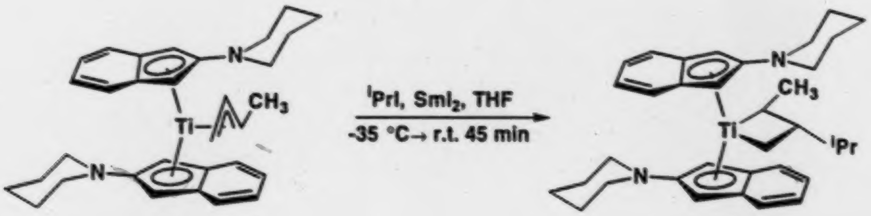
This radical trapping reactivity of crotyl complex **147** is significant since it is the first definitive experimental demonstration of our hypothesis that strong donor cyclopentadienyl ligands would facilitate central carbon alkylation at substituted η^3-allyl complexes. The milder conditions required for these reactions also suggest a more reactive metal center and, perhaps, greater odd-electron density on the crotyl ligand. It is possible that the low yields observed for these reactions are due to decomposition of the metallacyclobutane complexes during work-up rather than any inefficiency of the reaction. As determined for the *ansa*-bridged titanacyclobutane complexes **121a-c** and **122a** and **122b**, we believe this decomposition is initiated by β-hydride elimination at the α-methyl group (Scheme 2.19, above).

Rather disappointingly and contrary to expectations, however, addition of other organic radicals to crotyl complex **147** failed to give central carbon alkylation products. For instance, the bulky *tert*-butyl radical, generated by SmI_2 using either 2-bromo-2-methylpropane or 2-chloro-2-methylpropane, gave only dark green intractable material. Addition of allyl and crotyl radicals gave unidentifiable dark red-brown diamagnetic products, possibly including the Ti(IV) dihalide complex. The lack of central carbon alkylation reactions of these radicals may be due to unfavorable steric interactions in case of *tert*-butyl radical or rapid dimerization/disproportionation of the allyl radicals. Alternative radical generating strategies, *e.g.*, the Ti(III)-mediated epoxide opening, also failed to give tractable material.

The exact role played by the phenyl groups in the ancillary ligand of crotyl complex **147** in determining the radical trapping reactivity is uncertain. It is known that these substituents can be both electron-withdrawing or electron-donating depending on the demand for electron density by the system in question. Presumably, the electronic unsaturation of this 17-electron titanium(III) complex may cause these phenyl substituents to act as electron donors, further facilitating the radical trapping potential of these complexes.

2. Bis(2-piperidinoindenyl)titanium Crotyl and Cinnamyl Complexes.

The sterically less congested but presumably less electron donating bis(2-piperidinoindenyl)titanium crotyl and cinnamyl complexes, **150** and **151**, also undergo radical alkylation. Thus, treatment of a 1 : 1 mixture of crotyl complex **150** and SmI$_2$ with one equivalent 2-iodopropane affords the 3-isopropyl-2-methyl titanacyclobutane complex **153a** in moderate isolated yield (Equation 2.22). Similar to titanacyclobutane complexes **152a-c**, thermal instability precludes complete structural assignment; however, the ^{1}H NMR spectrum clearly indicates resonances characteristic of a 3-alkyl-2-methyltitanacyclobutane complex. The resonances defining the four-membered metallacycle are observed at δ 2.53 (t, J = 10.0 Hz) and 0.33 (dd, J = 10.0 Hz) (α-methylene hydrogen atoms), -0.24 (β-methine hydrogen atom) and 1.70 (dq, J = 12.8, 6.4



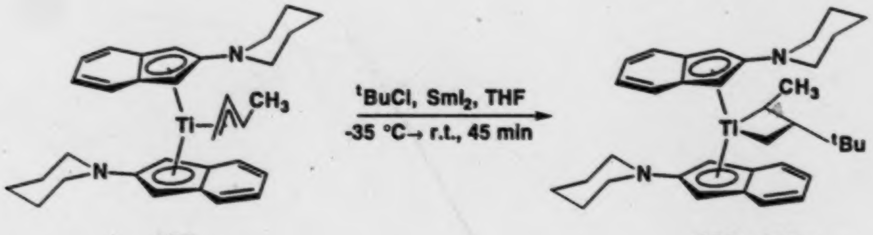
(2.22)

150

153a (69%)

Hz) (α-methine hydrogen). The 2.2 ppm difference in chemical shift between the two α-methylene hydrogen atoms is rather surprising, since the chemical shift differences observed for other 2,3-disubstituted metallacycles is about 0.4 ppm. This suggests that the α-methylene hydrogen with the high field signal is located in a highly shielded environment, possibly under one of the indenyl ligands where it would experience significant anisotropic shielding. The resonances assigned to the substituents on the metallacyclic ring are observed at δ 1.86 (d, J = 6.4 Hz) for α-methyl group, 1.18 (d, J = 6.6 Hz) and 1.08 (d, J = 6.6 Hz) for the diastereotopic isopropyl methyl groups and 1.96 (multiplet) for the isopropyl methine proton. The top-to-bottom and side-to-side dissymmetry of complex **153a** is established by the four one-hydrogen signals at δ 5.42 (d, J = 2.0 Hz), 5.24 (d, J = 2.1 Hz), 4.80 (brs) and 4.66 (brs) assigned to the inequivalent methine hydrogen atoms in the five-membered ring of the indenyl ligands. The multiplets between δ 7.43 and 6.85, assigned to the eight methine hydrogen atoms in the indenyl benzo-rings, and signals at δ 2.84, 2.70, 1.37 and 1.26, assigned to the methylene hydrogen atoms of the two piperidino substituents, further supports the structure assigned to complex **153a**.

In contrast to complex **147**, the large *tert*-butyl radical successfully adds to complex **150**, possibly reflecting the greater steric accessibility in the indenyl template. Thus, under standard conditions, 3-*tert*-butyl -2-methyl titanacyclobutane **153b** is isolated in low yield (Equation 2.23). Complete characterization of complex **153b** was not possible,

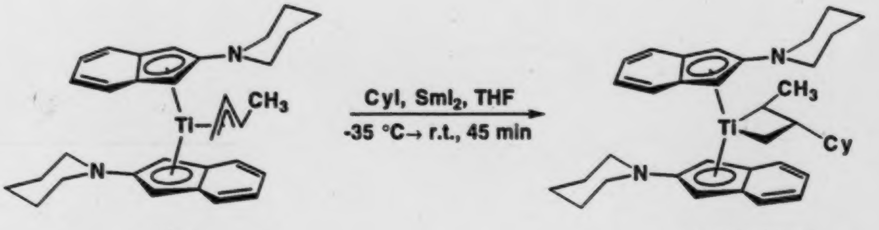


150 **153b (36%)**

(2.23)

since most of the characteristic ^1H NMR signals characterizing the four-membered ring overlap with signals for the piperidino methylene protons. A multiplet at δ 2.23 (α-methine hydrogen atom) and the high field multiplet at δ -0.11 (β-methine hydrogen atom) are nonetheless readily observable. The expected doublet for the α-methyl group appears at δ 1.81 (J = 6.5 Hz), while a nine-hydrogen singlet at δ 1.13 is assigned to the β-*tert*-butyl group. Similar to complex **153a**, typical resonances for the ancillary ligands in complex **153b** are observed in the downfield region of the spectrum.

Cyclohexyl radical is also effectively trapped by complex **150** to give the 2,3-disubstituted titanacyclobutane **153c** in good isolated yield (Equation 2.24). Partial characterization of complex **153c** was accomplished by ^1H NMR spectroscopy in a similar manner to complexes **153a** and **153b**.



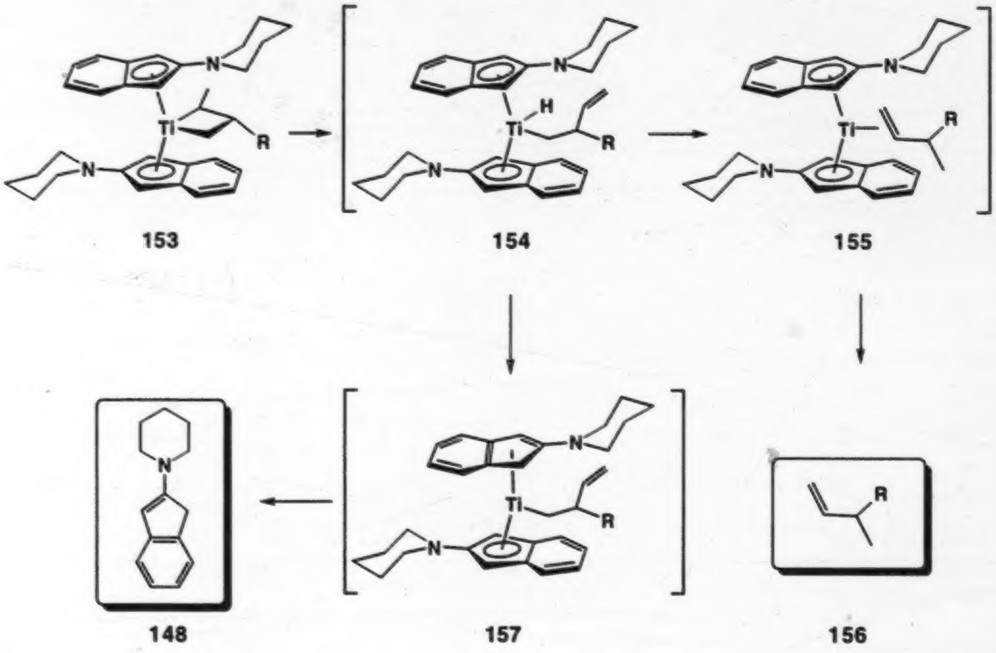
150 **153c (70%)**

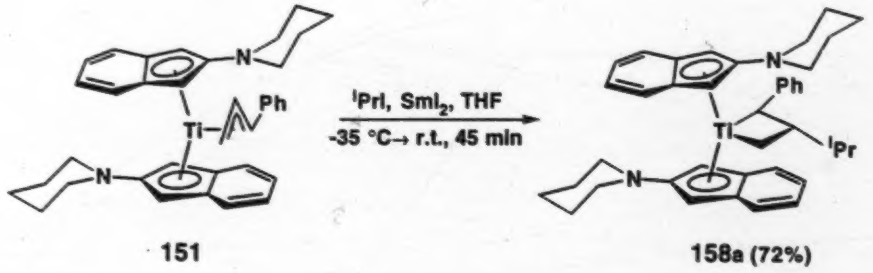
(2.24)

Repeated attempts to obtain elemental or high resolution mass analyses of these complexes failed. The high resolution mass spectra showed only signals pertaining to the ancillary ligand, perhaps revealing some kinetic instability in these complexes. In fact, the titanacyclobutanes completely decompose in solution at room temperature over a 12-hour period to yield the starting ancillary ligand **148**, a terminal alkene, and a large amount of intractable material. This suggests the decomposition of these complexes go via a similar β-elimination pathway to that proposed for the *ansa*-bridged titanacyclobutane complexes (Scheme 2.29).

In a manner similar to crotyl complex **150**, the cinnamyl complex **151** undergoes facile central carbon radical alkylation to give corresponding titanacyclobutane complexes. Higher isolated yields of these complexes are obtained, presumably due to the greater thermal stability of the α-phenyl framework. Thus, the addition of 2-iodopropane to complex **151** and SmI_2 gives 3-isopropyl-2-phenyl titanacyclobutane **158a** in good isolated yield (Equation 2.25).

Scheme 2.29. Possible Decomposition Pathway of Titanacyclobutanes

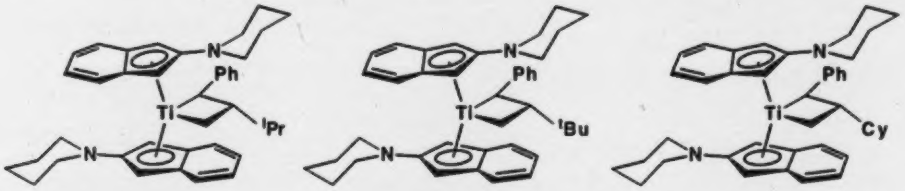

N
Ti
R
H
153
154
155
148
157
156


N
Ti
Ph
ⁱPrI, SmI₂, THF
-35 °C→ r.t., 45 min
ⁱPr
151
158a (72%)

(2.25)

Structural characterization of complex **158a** is based on analysis of the spectroscopic data and is more comprehensive than for complexes **153a-c**. At room temperature, the ^{1}H NMR spectrum revealed that complex **158a** is fluxional, giving a spectrum with several broad featureless multiplets. As a consequence, the spectrum was re-acquired at 70 °C, above the fast exchange limit, and is presented in Table 2.4. The temperature-averaged spectrum of **158a** shows resonances characteristic of the four-membered titanacyclobutane ring: δ 2.61 (dd, J = 10.0 Hz) and 0.04 (dd, J = 10.0 Hz) for the α-methylene protons, 0.84 (multiplet) for the β-methine proton, and 2.48 (d, J = 11.6 Hz) for the α-methine proton. As observed for α-methyl complexes **153a-c**, the chemical shift differences between the signals assigned to the two α-methylene hydrogen atoms remains at 2.2 ppm, suggesting structural similarity between the crotyl and cinnamyl adducts. Another noteworthy feature is the pronounced downfield shift of the signal for the β-methine hydrogen, as compared to other disubstituted titanacyclobutanes (approximately +1.00 ppm shifted from the usual upfield position). Resonances at δ 7.23 (dd, J = 8.1, 7.3 Hz), 7.10 (d, J = 7.6 Hz) and 6.87 (d, J = 7.2 Hz) are assigned to the methine protons on the α-phenyl substituent. The isopropyl substituent is indicated by two doublets at δ 1.04 (J = 6.6 Hz, 3H) and 0.95 (J = 6.6 Hz, 3H), assigned to the diastereotopic methyl groups and a multiplet at δ 1.54, assigned to the methine proton. Homonuclear decoupling and difference NOE measurements enabled the relative orientations of key protons to be determined, in particular, the *trans* orientation of the phenyl and isopropyl substituents in the titanacyclobutane ring (Figure 2.2). Characteristic ^{13}C NMR resonances identifying the titanacyclobutane ring are observed at δ 86.5 and 82.7 for the α-methine and methylene carbons, respectively, and the high field signal at δ 34.6 for the β-methine carbon atom. The similarity in the chemical shift of the α-methylene carbon to that of the normally deshielded α-methine carbon may be due to anisotropic deshielding from one of the indenyl ligands. Analytically pure red-brown

Table 2.4. ^{1}H NMR Resonances of Titanacyclobutane Complexes **158a - 158c**, 70 °C.



	R = ^{i}Pr, **158a** δ (m, J, I)*	R = ^{t}Bu, **158b** δ (m, J, I)*	R = Cy, **158c** δ (m, J, I)*
Ti-CH$_2$	2.61 (t, 10.0, 1H); 0.04 (t, 10.0, 1H)	2.71 (t, 10.0, 1H); -0.24 (brs, 1H)	2.63 (t, 10.0, 1H); 0.07 (dd, 10.0, 1H)
Ti-C$\underline{H}$(Ph)	2.48 (d, 11.6, 1H)	3.53 d, 11.7, 1H	2.41 (d, 11.1, 1H)
β-CH	0.84 (m, 1H)	1.15 (m, 1H)	0.80 (m, 1H)
Ph	7.23 (dd, 8.1, 7.3, 2H); 7.10 (d, 7.6, 2H); 6.87 (d, 7.2, 1H).	7.21 (brs, 2H); 7.15 (brs, 1H); 6.87 (m, 2H)	7.37 (d, 7.0, 1H); 7.23 (dd, 7.6, 7.5, 1H); 7.10 (d, 7.7, 1H)
CH$_{(In)}$	7.36 (dd, 6.7, 1.0, 1H); 7.34 (dd, 8.8, 1.0, 1H); 7.30 (m, 1H); 7.05 (ddd, 7.7, 7.5, 1.0, 1H); 6.92 (m, 2H); 6.73 (ddd, 7.7, 7.5, 1.1, 1H); 6.45 (dd, 8.4, 0.6, 1H); 5.40 (d, 2.3, 1H); 5.27 (d, 2.4, 1H); 5.03 (d, 2.1 Hz, 1H); 4.80 (d, 2.1, 1H)	7.41 (dd, 6.6, 2.0, 1H); 7.35 (d, 8.0, 1H); 7.33 (dd, 6.6, 2.4, 1H); 6.99 (ddd, 7.2, 6.7, 1.0, 1H); 6.87 (m, 2H); 6.64 (ddd, 7.1, 6.8, 1.0, 1H); 6.14 (dd, 8.4, 1H); 5.85 (d, 2.3, 1H); 5.51 (brs, 1H); 4.79 (brs, 1H); 4.71 (brs, 1H)	7.36 (d, 7.8, 1H); 7.35 (dd, 7.8, 7.0, 1H); 7.31 (d, 7.7, 1H); 7.06 (dd, 8.9, 7.5, 1H); 6.90 (m, 2H); 6.75 (dd, 7.6, 7.3, 1H); 6.47 (d, 8.3, 1H); 5.40 (d, 2.0, 1H); 5.26 (d, 2.1, 1H); 5.04 (brs, 1H); 4.78 (brs, 1H)
R	1.54 (m, 1H); 1.04 (d, 6.6, 3H); 0.95 (d, 6.6, 3H)	1.03 (s, 9H)	1.85 (m, 1H) 1.70 (m, 3H) 1.49 (m, 4H) 1.31 (m, 3H)

* δ = chemical shift, m = multiplicity, J = J$_{HH}$ in Hz, and I = integral.

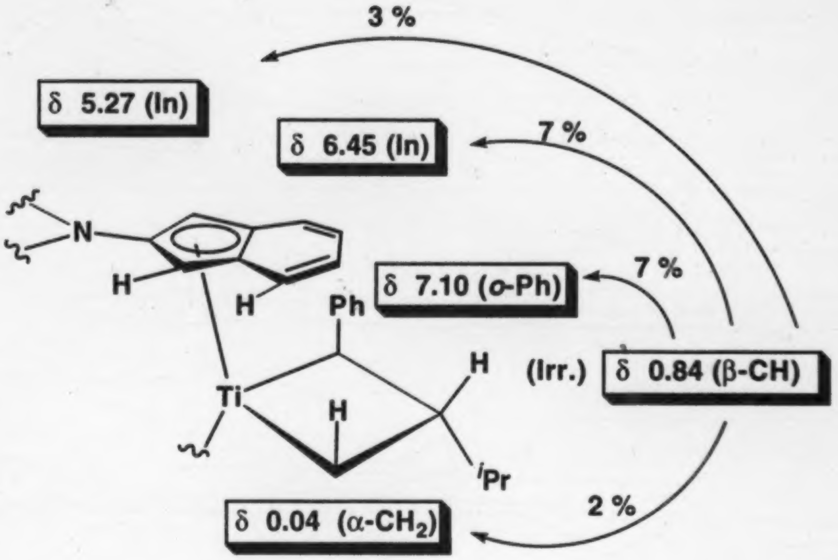
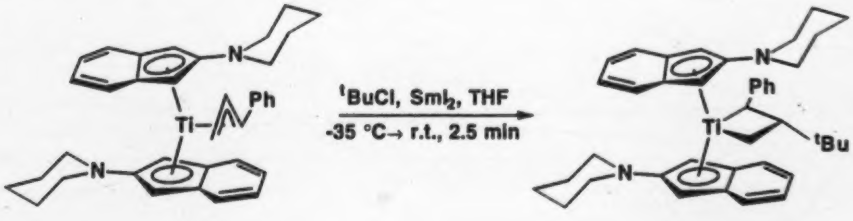

3 %
δ 5.27 (In)
δ 6.45 (In)
7 %
N
H
H
Ph
δ 7.10 (o-Ph)
7 %
H
(Irr.)
δ 0.84 (β-CH)
Ti
H
ⁱPr
2 %
δ 0.04 (α-CH₂)

Figure 2.2. Selected NOE Results for Titanacyclobutane **158a**

needles of complex **158a** (as an etherate) were obtained from a cold (-35 °C) ether solution layered with hexane.

Cinnamyl complex **151** also efficiently traps the bulky *tert*-butyl radical, giving the expected central carbon alkylation product 3-*tert*-butyl-2-phenyl titanacyclobutane **158b** in high yield (Equation 2.26). Characterization of this complex was accomplished in a similar manner to complex **158a**. Complete ^{1}H NMR spectroscopic data for complex


N
Ti
Ph
N
ᵗBuCl, SmI₂, THF
-35 °C→ r.t., 2.5 min
N
Ph
Ti
ᵗBu
N

(2.26)

151

158b (88%)

158b at 70 °C are presented in Table 2.4, confirming the structural similarity to isopropyl adduct **158a**. The one-bond ^{13}C-^{1}H heteronuclear correlated spectrum confirmed the spectroscopic assignments for complex **158b**. Analysis of this spectrum confirmed that the signals at δ 2.71 and -0.24, corresponding to the α-methylene protons, are correlated to a single carbon resonance at δ 80.7, assigned to the α-methylene carbon atom. Analytically pure red-brown needles of complex **158b** (as an etherate) were obtained from a cold (-35 °C) ether solution layered with hexane.

The fluxionality of complex **158b** was probed by variable temperature ^{1}H NMR spectroscopy to gain an appreciation of the conformational dynamics of this complex. At 70 °C, the ^{1}H NMR spectrum of complex **158b** in toluene-d_8 shows sharp signals that were readily assigned (*vide supra*). A considerable broadening of the spectrum resulted on cooling to room temperature, leaving only a few resonances clearly defined: a doublet at δ 3.53 (α-methine proton) and triplet at δ 2.71 (deshielded α-methylene proton), suggesting that the fluxionality is away from the titanacyclobutane ring. Cooling the sample to 0 °C gave a spectrum with only broad featureless multiplets, indicating that the rate of conformational interconversion of complex **158b** is similar to the NMR time scale. On further cooling to -40 °C, the spectrum shows two distinct sets of signals in a 2 : 1 ratio, indicating the presence of two non-interconverting conformers of complex **158b**. Significantly, the signal for one of the α-methylene protons in the major isomer is shifted markedly upfield (-1.38 ppm) from that observed in the high temperature spectrum. These observations suggest that the orientation of the indenyl ligands in the major conformer is as illustrated (Figure 2.3B) in which one α-methylene proton resides in the shielding environment of the lower indenyl ligand. Structure A (Figure 2.3) is suggested for the structure of the minor conformer, in which the same α-methylene proton experiences less shielding from the bottom indenyl ring.

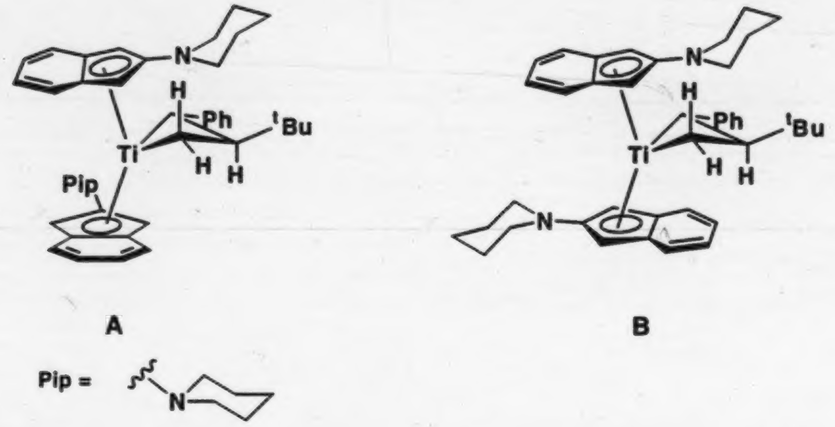
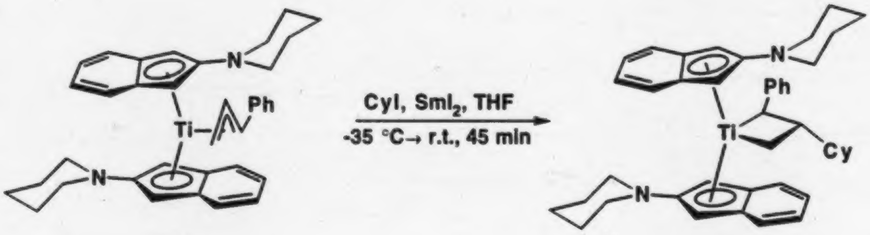


Figure 2.3. Proposed Structures of Non-Interconverting Conformers of 158b

Complex **151** is also an excellent radical trap for the cyclohexyl radical, providing 3-cyclohexyl-2-phenyl titanacyclobutane **158c** in high isolated yield (Equation 2.27). The structural assignment of complex **158c** is based on spectroscopic data closely

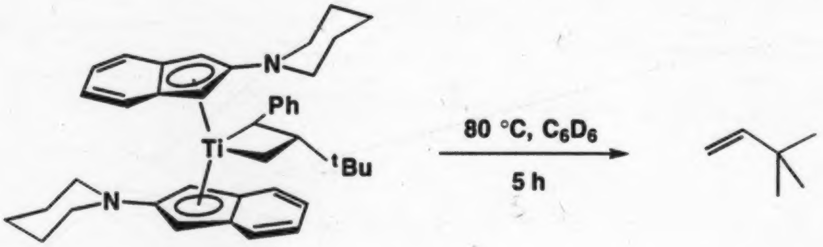


151 **158c** (80%) (2.27)

analogous to titanacyclobutanes **158a** and **158b**, as presented in Table 2.4. Analytically pure red-brown needles of complex **158c** (as an etherate) were obtained from a cold (-35 °C) ether solution layered with hexane.

The crotyl and cinnamyl titanocene complexes **150** and **151** undergo central carbon radical alkylation efficiently despite the lower electron-donor strength of the indenyl ligands (*vide supra*). It is known that the *benzo*-ring reduces the donor strength of the indenyl ligand due to the aromaticity of its six π-electrons.[147] The successful alkylation of these complexes, therefore, strongly suggests that the mesomeric interaction of the nitrogen lone pair with the indenyl ligand is mainly responsible for promoting central carbon alkylation in these systems. Efforts are currently underway in the Stryker group to investigate the radical trapping capabilities of aminotitanocene η^3-allyl complexes lacking these conjugated π-systems as substituents on the ancillary ligands.[148]

α-Phenyl titanacyclobutane complexes **158a-c** are much more thermally stable than α-methyl complexes **153a-c**. The former complexes do not show any sign of decomposition when heated to 70 °C for an extended period (9-12 h); however, slow decomposition begins above 80 °C, producing a terminal alkene. For example, β-*tert*-butyl titanacyclobutane **158b** yields 3,3-dimethylbutene exclusively, along with organometallic decomposition material (Equation 2.28). This suggests that the [2 + 2] cycloreversion reaction is highly regioselective. Efforts continue to trap the expected titanium phenylvinylidene intermediate.



158b **159**

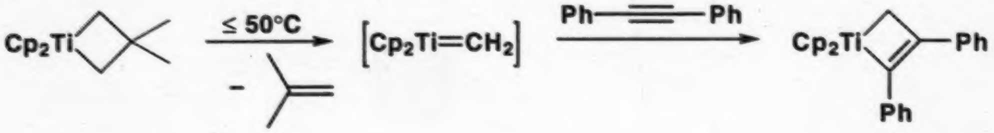
(2.28)

CHAPTER 3. RESULTS AND DISCUSSION: FUNCTIONALIZATION OF METALLACYCLOBUTANE COMPLEXES

3.1. Introduction

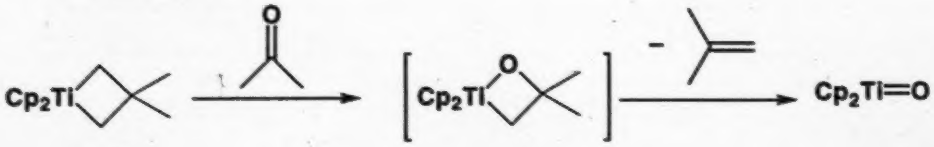
In an effort to develop new methodologies for the efficient synthesis of useful organic molecules, a fundamental study of the functionalization of titanacyclobutane complexes using small unsaturated organic compounds was undertaken. Bis(cyclopentadienyl)titanacyclobutane complexes are thermally sensitive, undergoing facile cycloreversion to give an olefin along with a highly reactive titanium methylidene complex, the reactive intermediate in olefin metathesis (Scheme 3.1).[149] This intermediate can be trapped by various unsaturated compounds (alkenes, alkynes and ketones). For example, the reaction with diphenylacetylene gives the titanacyclobutene complex **162** (Scheme 3.1),[150] while the reaction with ketones initially gives the unstable oxatitanacyclobutane complex **163**, which further reacts to produce the corresponding olefin (a 'Wittig'-type product) and polymeric titanocene oxide **164** (Scheme 3.2).[150]

Scheme 3.1



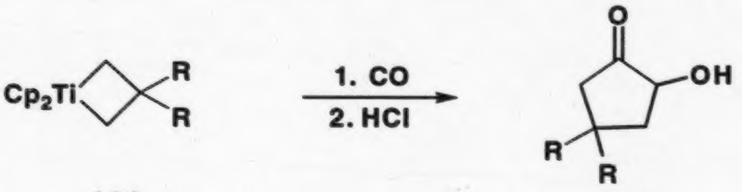
160 **161** **162**

Scheme 3.2



160 **163** **164**

Another reactivity pattern involving titanacylobutane complexes is ring expansion via migratory insertion of unsaturated polar molecules into the titanium carbon σ-bonds.[150] For instance, Grubbs, have reported that titanacyclobutane complexes **160** give the α-hydroxycyclopentanones **165** in modest yield when treated with CO followed by protonolysis (Equation 3.1).[150] Based on the organic compounds isolated after protonolysis, this reaction is thought to go via double insertion of CO followed by rearrangement to give the enediolate complexes.[151] Support for the double CO insertion into the metal-carbon bonds in these complexes is found in the reactivity of $Cp^*_2ZrMe_2$ **166**, thoroughly investigated by Bercaw (Scheme 3.3).[151,152]

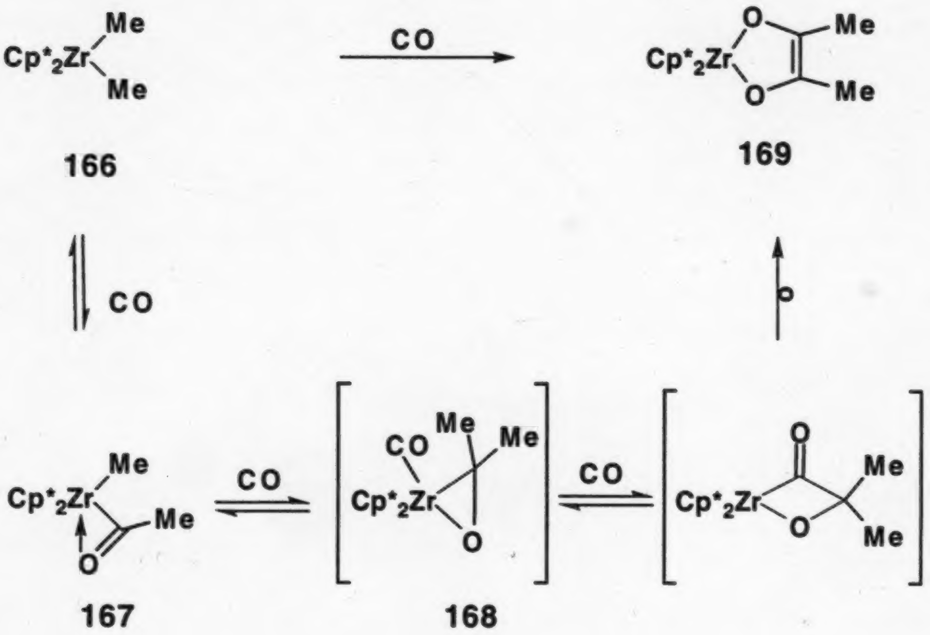


160 **165**

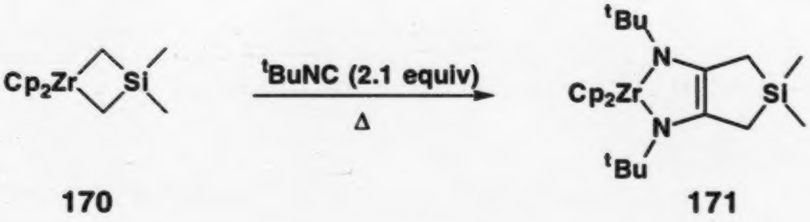
(3.1)

Although there are several mechanistic possibilities,[151-153] one suggestion invokes a methyl migration to the carbonyl carbon of the η^2-acetyl ligand to give the η^2-acetone adduct **168**.[152,153] Subsequent CO insertion into the η^2-acetone adduct, followed by a 1,2-methyl shift affords the enediolate **169** (Scheme 3.3). Recently, Petersen has provided strong support for an alternative mechanism from his investigation of the 1-sila-3-zirconacyclobutane complex **170**.[154-156] This mechanistic study focused on the insertion of the isoelectronic isonitrile to give the corresponding enediaminate complex **171** (Equation 3.2), analogous to enediolate complex **169**. Intermediates on the reaction pathway to the enediaminate complex could be isolated and characterized (Scheme 3.4). Addition of one equivalent of ^{13}C-labeled *tert*-butyl isonitrile to complex **170** yields the iminoacyl complex **172**, which reacts with a second equivalent of isonitrile to give the six-membered metallacyclic complex **173** (Scheme 3.4).[157,158] The position of the labeled carbon atom showed that the second isonitrile inserts into the Zr-C(iminoacyl) bond.[155] Thermolysis of complex **173** results in the quantitative formation of

Scheme 3.3


Cp*$_2$Zr
Me
Me
CO
O
Me
Me
166
169
CO
Me
Me
O
167
CO
CO
Me
Me
O
168
CO
O
Me
Me
O

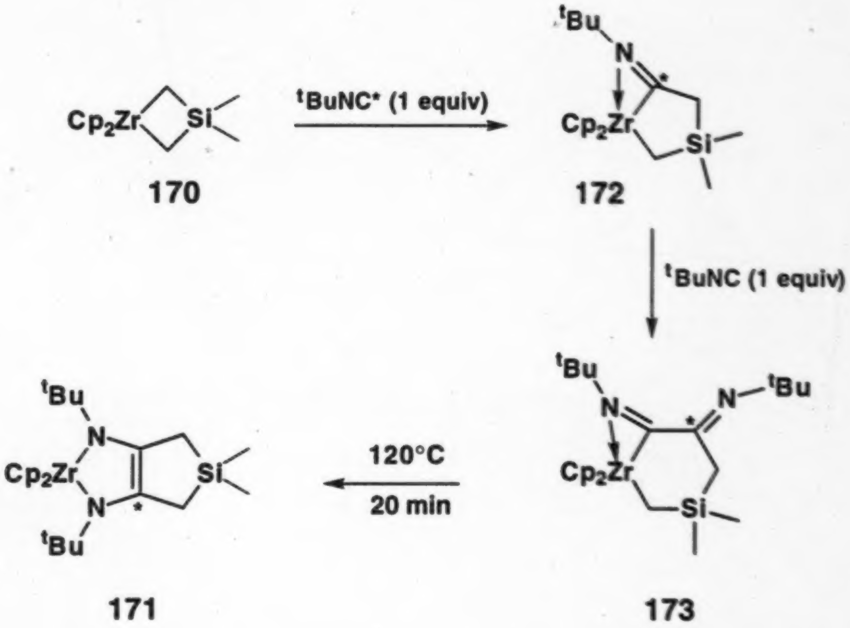
enediaminate complex **171**. Further evidence for this reactivity was reported recently,[156] which demonstrated that addition of a third equivalent of isonitrile was possible, giving the 7-membered ring adducts **174** and **175**, containing three consecutive isonitrile units (Scheme 3.5).


Cp$_2$Zr
Si
^{t}BuNC (2.1 equiv)
Δ
^{t}Bu
N
N
^{t}Bu
Cp$_2$Zr
Si
170
171

(3.2)

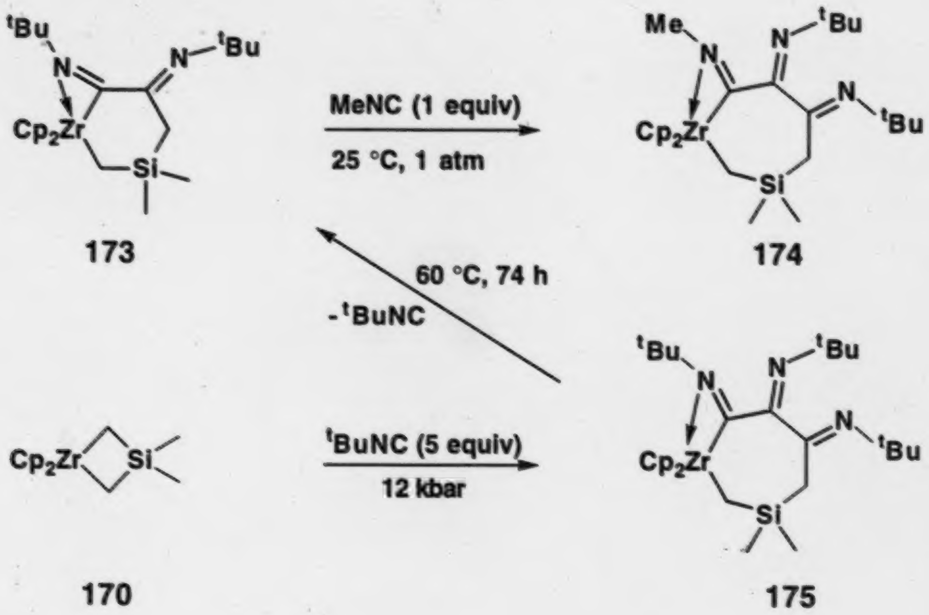
Another ring expansion reaction characteristic of these 1-sila-3-zirconacyclobutane complexes has recently been reported.[154,158,159] Typical reactivity observed involves the insertion of CO into the zirconium-carbon bond, which is followed by a 1,2-silyl rearrangement to form zirconium enolate complexes containing one or two exocyclic double bonds (Scheme 3.6).[154] When complex **176** is treated with CO at room temperature, there is stepwise insertion of two equivalents of CO to give the enolate **177** and dienolate **178** complexes. A similar reactivity pattern is observed for the insertion of methyl isonitrile into these complexes, leading to the isolation of enamide complexes.[158,159]

Scheme 3.4



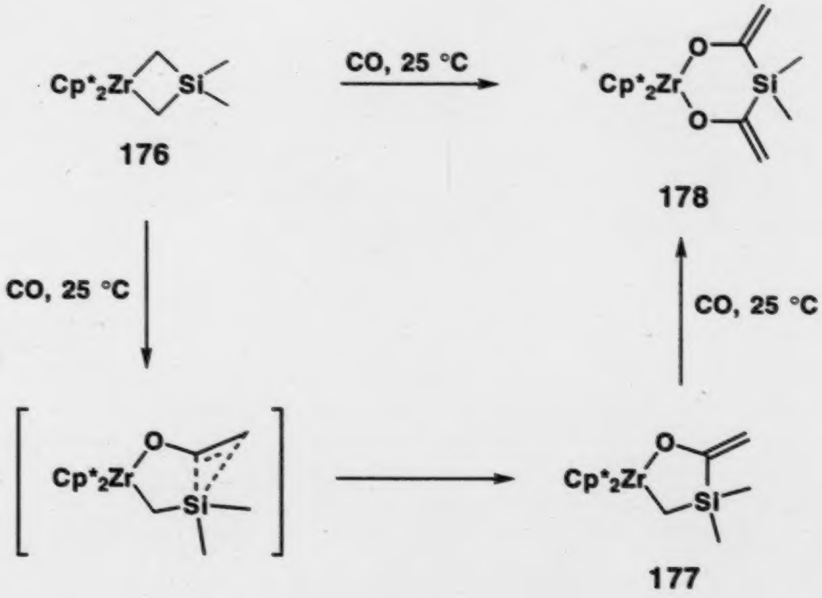
Apart from these two investigations, there has been very little work done on developing such ring expansion reactions for the functionalization of metallacyclobutane complexes and the synthesis of organic compounds. This is because there are not many good ways to make titanacyclobutane complexes.[81] In particular, there has been no

Scheme 3.5



173
174
175
170
MeNC (1 equiv)
25 °C, 1 atm
60 °C, 74 h
-^{t}BuNC
^{t}BuNC (5 equiv)
12 kbar
Cp$_2$Zr
Si
N
Me
^{t}Bu

Scheme 3.6



176
177
178
CO, 25 °C
CO, 25 °C
CO, 25 °C
Cp*$_2$Zr
Si
O

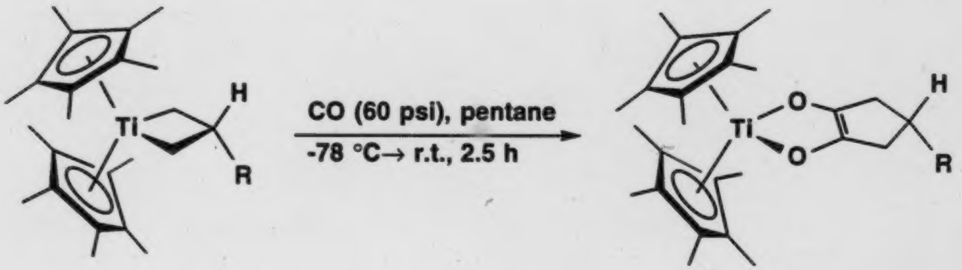
report on single insertion reactions of unsaturated organic molecules to form four-membered carbocycles subsequent to demetallation. This reactivity is commonly observed for insertions into the homologous metallacyclopentane complexes, providing five-membered carbocycles cleanly and in high yield.[41,150,160-185]

Consequently, the functionalization of various titanacyclobutane complexes via ring expansion was investigated using polar unsaturated compounds, focusing on the use of carbon monoxide, isonitriles and simple carbonyl compounds. The titanacyclobutane complexes used for this investigation were prepared via central carbon alkylation of both cationic titanium (IV)[25,39] and neutral titanium (III)[39,42] η^3-allyl complexes, including some 2,3- disubstituted titanacyclobutane complexes.

3.2. Double Carbon Monoxide Insertion Reactions of Titanacyclobutane Complexes

The reaction of carbon monoxide with various β-alkyl substituted bis(pentamethylcyclopentadienyl)titanacyclobutane complexes (**47a,b,e,g,i,j**) occurs efficiently to give cyclopentenediolate complexes (Scheme 3.7). The reaction is conducted optimally at -78 °C under 60 psi of CO pressure, followed by warming to room temperature over two hours, giving enediolate complexes **179a-f** in excellent isolated yields. Structural assignment of these complexes follows from analysis of the NMR spectroscopic data and from comparisons with previously reported data for analogous enediolate complexes.[150-152,154,172,173] The ^{1}H NMR spectrum of complex **179a**, for example, shows resonances for the protons of the cyclopentene ring as overlapping second-order multiplets at δ 2.60 and 1.25, while large singlets at δ 1.80 and

Scheme 3.7



	R
47a	Bn
47b	C_3H_5
47e	^{t}Bu
47g	^{i}Pr
47i	Ph(CH_3)CH
47j	H

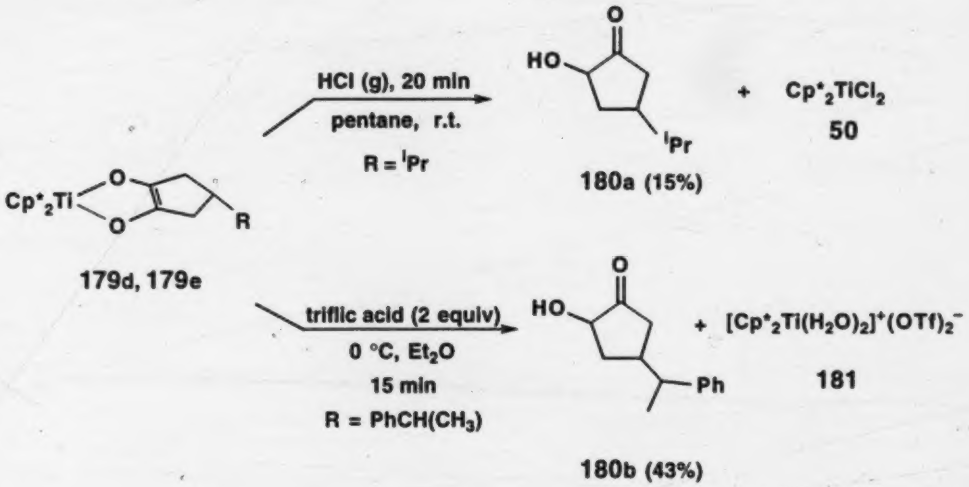
	R	yield (%)
179a	Bn	88
179b	C_3H_5	70
179c	^{t}Bu	75
179d	^{i}Pr	83
179e	Ph(CH_3)CH	90
179f	H	86

1.74 indicate the presence of inequivalent Cp* ligands, a consequence of the top-to-bottom dissymmetry of this complex. The presence of the benzyl moiety is indicated by a two-hydrogen multiplet at 2.73 for the benzylic methylene protons and a five-hydrogen multiplet at δ 7.1 for the phenyl protons. Further support for the proposed structure of **179a** is garnered from the gated decoupled ^{13}C NMR spectrum. The presence of four resonances for the Cp* ligands at δ 121.9 and 121.1 (quaternary carbon atoms) and 11.6 and 11.5 (methyl carbon atoms) confirms the top-to-bottom dissymmetry. The carbon atoms in the symmetric cyclopentene ring are indicated by a singlet at δ 147.0 for the olefinic carbons C-1 and C-5, a triplet at δ 38.9 for C-2 and C-4, and a doublet at δ 36.5 for C-3. The phenyl ring is denoted by typical signals for the ipso and methine carbon atoms, while the benzylic carbon is denoted by a triplet at δ 44.1. Confirmation of the elemental composition of **179a** is obtained from high resolution mass spectrometry. The characterization of the other enediolate complexes **179b-f** is accomplished in an entirely analogous manner. Except for the synthesis of the allyl permethylzirconocene cyclopentenediolate complex reported from this laboratory,[41] this is the first general investigation into the preparation of such complexes.

Several approaches to the demetallation of the 5-membered carbocycle were investigated. Protonolysis of complex **179d** with dry hydrogen chloride in pentane solution gives 2-hydroxy-4-isopropylcyclopentanone **180a** in very low yield (Scheme 3.8). A moderate improvement in yield is observed using trifluorosulfonic acid as the proton source (Scheme 3.8), but no further increase in efficiency could be attained. The poor efficiency of these reactions stands in contrast to protonolysis of bis(cyclopentadienyl)titaniumcyclopentenediolate complexes,[150,186,187] suggesting that the bulkier Cp* ligands in our system inhibits the protonolysis, allowing non-productive reactivity pathways to be accessed.

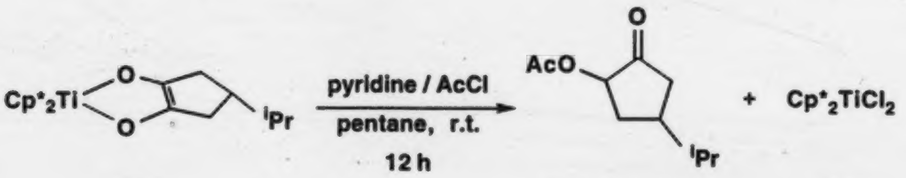
Structure assignment of the keto-alcohols rests on analysis of the spectroscopic data. Infrared absorption bands at 3340 and 1735 cm^{-1} are characteristic of the hydroxyl group and a five-membered cyclic ketone in **180a**. The ^{1}H NMR resonance at δ 4.13 (ddd, J = 11.8, 8.2, 2.4 Hz), is consistent with the hydroxymethine proton at C-2, while the three-hydrogen resonances at δ 0.94 and 0.92 for the diastereotopic methyl groups and multiplet at δ 1.51 for a methine proton confirm the presence of the isopropyl substituent. Complex multiplets at δ 2.52, 1.62 and 1.32 account for the other five protons in the cyclopentanone ring. Even though the relative stereochemistry of the hydroxyl and isopropyl substituents could not be determined due to the complex nature of the latter multiplets, only a single diastereomer is formed.

Scheme 3.8


HCl (g), 20 min
pentane, r.t.
R = ^{i}Pr
HO
O
^{i}Pr
180a (15%)
+ $Cp^*_2TiCl_2$
50
Cp^*_2Ti
O
O
R
179d, 179e
triflic acid (2 equiv)
0 °C, Et_2O
15 min
R = PhCH(CH_3)
HO
O
Ph
180b (43%)
+ $[Cp^*_2Ti(H_2O)_2]^+(OTf)_2^-$
181

Structure assignment of compound **180b** is accomplished in a manner similar to **180a**. The characteristic infrared absorption bands at 3343 and 1746 cm^{-1} in the infrared spectrum of **180b** indicate the presence of a hydroxyl group and five-membered ketone. As expected, the ^{1}H NMR spectrum of cyclopentanone **180b** shows the presence of two diastereomers, clearly revealed by the two hydroxymethine signals at δ 4.15 and 4.04 in a ratio of 1 : 1.3. The diastereomers are expected to be different at the benzylic position since the phenylethyltitanacyclobutane complex, **47i**, the precursor of cyclopentenediolate **179e**, is epimeric at the benzylic carbon.[39] Unambiguous assignment of the other signals in the spectrum was not possible due to extensive overlapping of signals. The relative stereochemistry of the two substituents in the five-membered ring could not be determined, again due to overlapping signals. High resolution mass spectrometry of the diastereomeric mixture confirmed the elemental composition of **180b**.

Acetylation has also been investigated as a means of removing the carbocyclic moiety from the organometallic template (Equation 3.3). This process, unfortunately, is very inefficient, giving only a low yield of 2-acetoxy-4-isopropylcyclopentanone **182**. The spectroscopic features of this compound are similar to the α-hydroxy analogue, except for the expected downfield shift of the signal for the hydroxymethine proton at C-2 from 4.13 ppm to 5.10 ppm, and the additional singlet at δ 2.13 for the methyl group of the acetyl moiety. IR spectroscopy confirms the presence of two bands at 1757 cm^{-1} and 1739 cm^{-1} for the carbonyl groups of the ketone and ester moieties, respectively. The other spectroscopic data fully supports the assigned structure. High resolution mass spectrometry confirms the elemental composition of compound **182**.

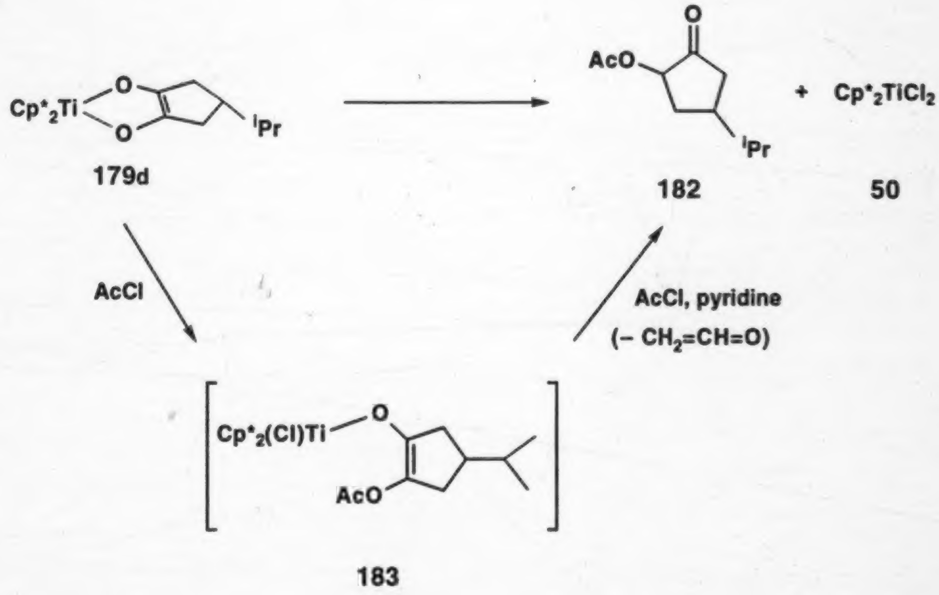


(3.3)

179d **182** (25%) **50**

The mechanism of this reaction is not known, but reaction of the cyclopentenediolate **179d** and acetyl chloride to give intermediate **183** is most likely the first step (Scheme 3.9). The subsequent transformation of **183** is possibly mediated by pyridine and another equivalent of acetyl chloride to give keto-ester **182** and the dichloride complex **50**, along with ketene as a byproduct.

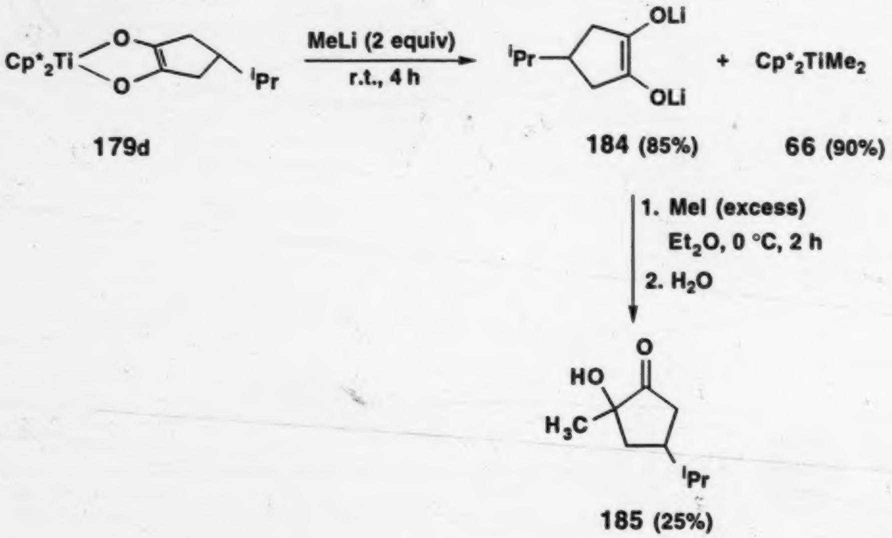
Scheme 3.9



An efficient demetallation of the 5-membered carbocycle can be achieved by transmetallation to lithium. Thus, treatment of the enediolate complex with excess methyllithium gives the titanocene dimethyl complex **66** and the liberated dilithium enediolate **184** (Scheme 3.10). Subsequent alkylation of the enediolate with methyl iodide gives 2-hydroxy-3-isopropyl-2-methylcyclopentanone **185**, but consistently in low yield. Alkylation of this class of compounds with larger electrophiles is well established and is useful for the synthesis of important organic materials, including prostaglandins.[188-191]

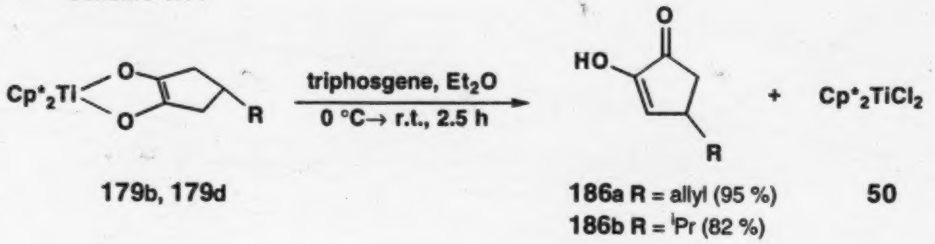
An alternative approach to demetallation was investigated, using triphosgene, reported to demetallate acyclic bis(cyclopentadienyl)titanium(pentenediolates) to give cyclic carbonates.[186] Surprisingly, none of the expected carbonates are formed; instead, the exclusive formation of 2-hydroxy-2-cyclopentenones **186a** and **186b** was observed upon treatment with one equivalent of triphosgene at 0 °C (Scheme 3.11). Characterization of these compounds rests on comparisons of the spectroscopic data with that of previously reported cyclopentanedione tautomers.[192] Characteristic ^{1}H NMR features of these compounds include the downfield vinylic proton resonance at δ 6.5 (d, J = 2.9 Hz) as well as the other signals for the expected ABMX spin system at δ 2.5 and 2.14 for the geminal protons (J_{AB} = 19 Hz, with additional couplings) and a complex multiplet at δ 2.6 for the proton of the adjacent methine position.

Scheme 3.10

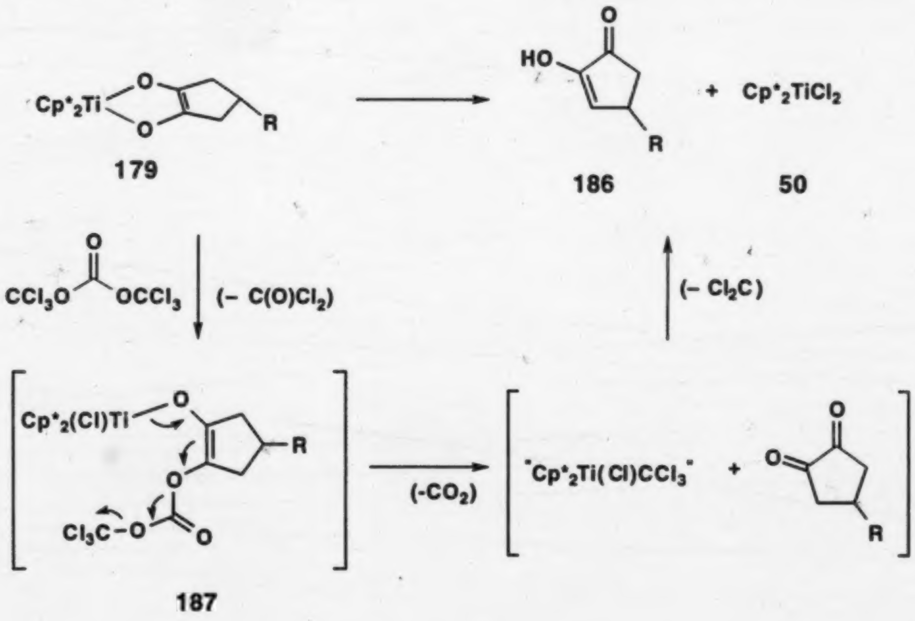


This is an unprecedented reaction, which results in an oxidative cleavage of one of the Ti-O bonds. It is possible that the bulky pentamethylcyclopentadienyl rings prevent carbonate formation from the expected intermediate **187** (Scheme 3.12), diverting this species into oxidative bond cleavage. It is plausible that the cleavage of the Ti-O bond in **187** proceeds as shown in Scheme 3.12 to give the 1,2-dione and a Ti(IV) monochloride species. Subsequent bond reorganization in this latter species would give the observed

Scheme 3.11


Cp*₂Ti
O
O
R
triphosgene, Et₂O
0 °C→ r.t., 2.5 h
HO
O
R
+
Cp*₂TiCl₂
179b, 179d
186a R = allyl (95 %)
186b R = ⁱPr (82 %)
50

Scheme 3.12

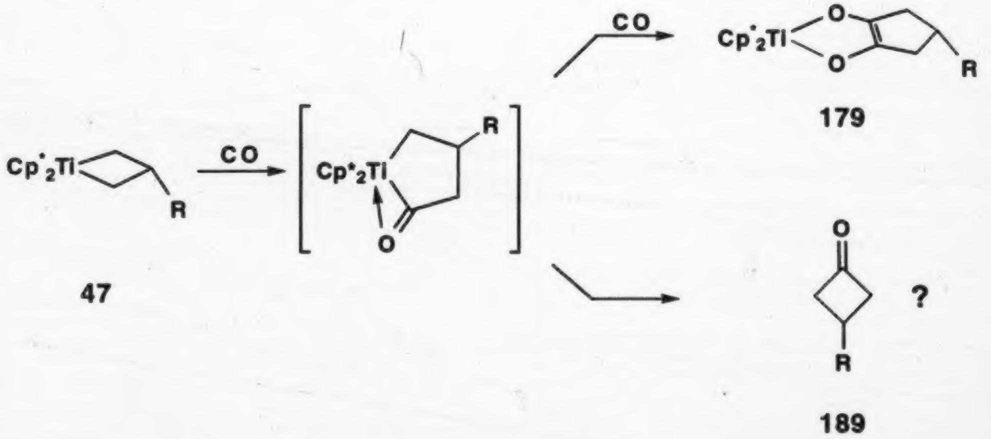

Cp*₂Ti
O
O
R
179
HO
O
R
186
+ Cp*₂TiCl₂
50
O
CCl₃O
OCCl₃
(– C(O)Cl₂)
(– Cl₂C)
Cp*₂(Cl)Ti
O
R
O
Cl₃C–O
O
187
(-CO₂)
"Cp*₂Ti(Cl)CCl₃"
+
O
O
R

dichloride complex, along with dichlorocarbene, which could react further. No mechanistic investigation of this reaction has yet been done. The high efficiency of this process makes it an attractive and potentially general demetallation strategy for other enediolate complexes.

3.3. A New General Synthesis of Cyclobutanones by Single Carbon Monoxide Insertion Into Titanacyclobutane Complexes

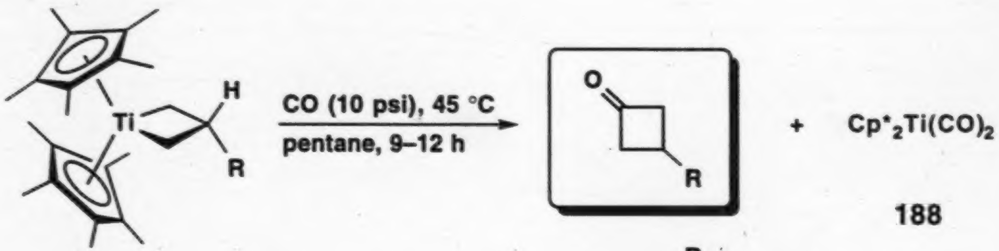
Considering that the double CO insertion reaction presumably occurs via the intermediate single insertion acyl complex proposed by Bercaw (Scheme 3.13),[151] we attempted to modify the reaction to stop it after the first CO insertion. We presumed that intramolecular reductive cyclization of the acyl intermediate might be promoted by a higher temperature and lower CO pressure. Thus, treatment of 3-isopropyl bis(pentamethylcyclopentadienyl)titanacyclobutane complex **47g** with 20 psig of CO at room temperature gives a mixture of the cyclopentenediolate **179d**, bis(pentamethylcyclopentadienyl)titanium dicarbonyl complex **188**[73,193,194] and 3-isopropylcyclobutanone **189e**. Under optimum conditions, the reactions gives cyclobutanone exclusively. Thus, treatment of various 3-alkyl titanacyclobutane complexes (**47a-d** and **47g**), pre-heated to 45 °C, with only 10 psig of CO provides the corresponding 3-alkyl cyclobutanones **189a-e** in high isolated yields (Scheme 3.14). Similar reaction conditions have been used for carbonylation of the analogous Cp_2TiR_2

Scheme 3.13



complexes, which give acyclic ketones.[195,196] A lower than expected yield of 3-allylcyclobutanone **189b** is obtained from the reaction of 3-allyl titanacyclobutane complex **47b**, perhaps due to some decomposition of the titanacyclobutane complex when it is heated prior to CO insertion.

Scheme 3.14



188

47a (Bn)
47b (C_3H_5)
47c (^{t}Bu)
47d (Ph_2CH)
47g (^{i}Pr)

	R
189a	Bn (85%)
189b	C_3H_5 (45%)
189c	^{t}Bu (quant)
189d	Ph_2CH (91%)
189e	^{i}Pr (quant)

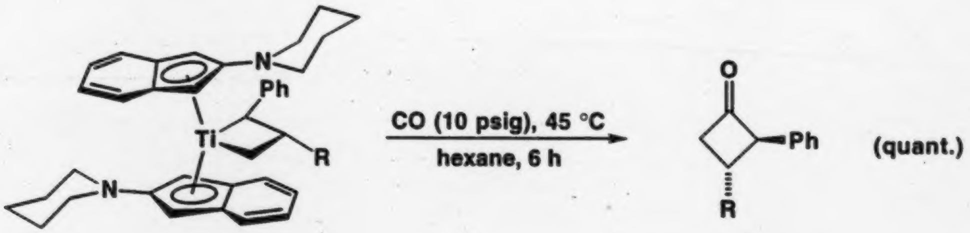
The structural assignments of the cyclobutanones follow from analysis of the spectroscopic data and from comparison with previously reported data for this class of compounds. The 3-benzyl- (**189a**),[197] 3-*tert*-butyl- (**189c**)[198] and 3-isopropylcyclobutanones (**189e**)[199] have been reported previously and show identical spectroscopic features to those in the literature. For 3-allyl cyclobutanone **189b**, previously unreported, the infrared spectrum shows a characteristic band at 1808 cm^{-1} (gas phase) for the carbonyl and a band at 1641 cm^{-1} establishing the presence of an olefinic moiety. Resonances at δ 5.44 and 4.83 in the ^{1}H NMR spectrum are characteristic of a terminal olefin, corroborating the IR data. A gated decoupled ^{13}C NMR spectrum fully supports the IR and ^{1}H NMR assignments, showing a singlet at δ 204.9, assigned to the carbonyl carbon, and signals at δ 136.2 (d, J = 150.6 Hz) and 116.0

(t, J = 155.4 Hz) for the olefinic carbons. The other spectroscopic data are fully consistent with the structure of cyclobutanone **189b**. Low resolution mass spectrometry supports its elemental composition. The structural assignment of 3-diphenylmethylcyclobutanone **189d** was determined similarly.

This is the first demonstration of a general synthesis of substituted cyclobutanones from carbonylation of metallacyclobutane complexes. In previous reports, however, a tantalum and a hafnium η^2-cyclobutanone complexes have been prepared by carbonylation of the corresponding metallacyclobutane complexes.[79,80] The mono carbonylation reaction reported here is similar to that observed for the analogous metallacyclopentane complexes.[151,177,180,181,183-185,200]

Some 2,3-disubstituted titanacyclobutane complexes also undergo carbonylation successfully. For example, treatment of 3-alkyl-2-phenyl bis(2-piperidinoindenyl)-titanacyclobutane complexes **158a-c** with CO under the established conditions gives 3-alkyl-2-phenylcyclobutanones **190a-c** quantitatively (Scheme 3.15). The expected titanium dicarbonyl complex is not observed and the fate of the titanium fragment remains unknown.

Scheme 3.15



158a - 158c

	R
190a	^{i}Pr
190b	^{t}Bu
190c	Cy

Structure assignment of the 2,3-disubstituted cyclobutanones **190a-c** again follows from analysis of the spectroscopic data. For example, the IR spectrum of cyclobutanone **190a** shows a band at 1781 cm^{-1}, characteristic of a cyclobutanone. The resonances at δ 4.08 (dt, J = 8.1, 2.4 Hz) and 2.34 (multiplet) in the ^1H NMR spectrum are assigned to the methine hydrogens at C-2 and C-3, while the resonances at δ 3.07 (ddd, J = 17.4, 8.8, 2.2 Hz) and 2.85 (ddd, *J* = 17.4, 8.1, 2.2 Hz) are assigned to the two diastereotopic hydrogens on C-4. Long-range coupling (between 0.9 and 2.0 Hz) has been noted previously for substituted cyclobutanones.[87,201,202] A *trans* orientation of the isopropyl and phenyl substituents is inferred from comparison of the coupling constants ($^3J_{HH}$). It is known that the *trans* coupling constant is generally smaller than the *cis* in a cyclobutanone ring.[87,201,202] It is expected, therefore, that the C-4 hydrogen attributed to the resonance at δ 2.85 is *trans* to the hydrogen at C-3 since the vicinal coupling constant is 8.1 Hz compared to 8.8 Hz for the other C-4 hydrogen. Accordingly then, the hydrogen at C-2 is tentatively assigned to be *trans* to the one at C-3 as a result of its identical vicinal coupling constant (8.1 Hz) compared to the hydrogen at C-4. A high resolution mass spectral analysis of **190a** confirms its elemental composition. Structural assignment of the **190b** and **190c** has been similarly accomplished.

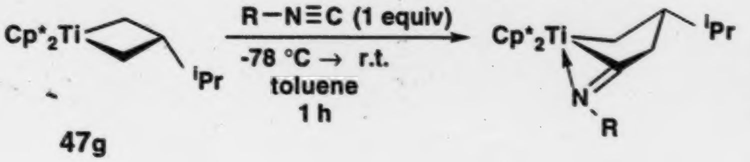
It is important to note that the regiochemistry of these 2,3-disubstituted cyclobutanones obtained here is opposite to that typically obtained from [2 + 2] cycloaddition of styrenes and dichloroketene.[203-205] This regiochemical complementarity, coupled with the efficiency of this reaction, makes it an attractive strategy for the synthesis of other highly substituted cyclobutanones of this type.

Several attempts to extend the carbonylation reaction to the 3-alkyl-2-methyl titanacyclobutane complexes failed. Only decomposition products are obtained when the 3-alkyl-2-methyltitanacyclobutane complexes **121a-c**, **152a,b**, and **153a,b** are subjected to carbonylation at any temperature. Rather surprisingly, the product mixtures resulting from carbonylation of the 3-alkyl-2-methyl bis(2-piperidinoindenyl)titanacyclobutane complexes contained free 2-piperidinoindene. The failure of these complexes to undergo carbonylation may be due to faster β-hydride elimination, a typical decomposition pathway for α-methyl titanacyclobutanes, compared to CO insertion.

3.4. Isonitrile Insertion Reactions of Titanacyclobutane Complexes

Alkyl isonitriles, isoelectronic analogues of CO, undergo more controlled insertion reactions, perhaps a function of the sterically significant nitrogen substituent. Hence, subjecting 3-isopropyl bis(pentamethylcyclopentadienyl)titanacyclobutane **47g** to one equivalent of cyclohexyl or *tert*-butyl isonitrile in toluene at low temperature yields dark green iminoacyl complexes **191a** and **191b** (Scheme 3.16). These complexes are isostructural to the acyl complexes postulated as intermediates in the CO insertion reaction.

Scheme 3.16



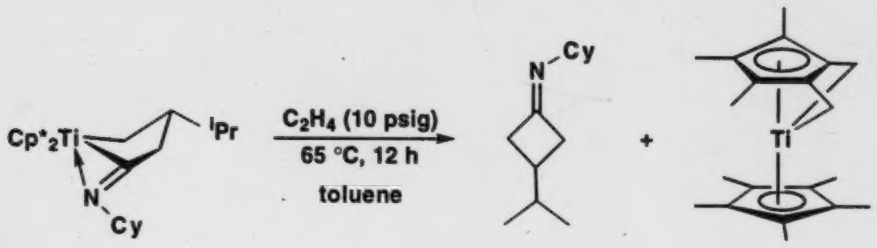
47g

	R
191a	ᵗBu (92%)
191b	Cy (90%)

The spectroscopic data of these complexes reveal some interesting features. Rather surprisingly, in the ^{1}H NMR spectrum of *tert*-butyl iminoacyl complex **191a**, the resonances for the diastereotopic α-methylene protons are separated by almost 4 ppm, with one appearing as a multiplet at δ 2.69 and the other at δ -1.15. The resonances for the other three protons in the five-membered ring are observed as second order multiplets at δ 1.97, 1.74 and 1.26. These assignments were confirmed by selected irradiation experiments, which showed the strong geminal coupling between the signals assigned to the α-methylene protons. Additional support for the proposed structure comes from the ^{13}C NMR spectrum, which features a highly deshielded carbon resonance at δ 233.8 assigned to the iminoacyl carbon atom. The infrared absorption band at 1588 cm^{-1} is consistent with other iminoacyl complexes of early transition metals.[155,156,158,162,164,206-210] The signal for the C-3 methylene carbon is observed as a triplet at δ 48.6, while the metal-bound methylene carbon (C-5) is observed as a doublet of triplets significantly further downfield at δ 66.4. The signal for the methine carbon of the five-membered ring is observed as a doublet at δ 37.3. The other resonances in the spectrum are readily assigned to the carbon atoms of the inequivalent ancillary ligands, the isopropyl and *tert*-butyl substituents, and are fully consistent with the assigned structure. An analytically pure sample of complex **191a** was obtained as dark brownish-green cubes from a cold (-35 °C) hexane solution.

The ^{1}H and ^{13}C NMR spectra of the cyclohexyl iminoacyl complex **191b** show similar resonances for the five-membered iminoacyl moiety, along with the additional signals for the cyclohexyl substituent. The resonances for the two α-methylene protons again appear as widely separated multiplets at δ 2.75 and -1.20, while the resonances for the other three protons in the five-membered ring are observed as complex second order multiplets at δ 2.05 and 1.65 (overlapping with the cyclohexyl signals). The remaining signals in the ^{1}H NMR spectrum are, along with the ^{13}C NMR data, fully consistent with the assigned structure for **191b**. Quite remarkably, however, the infrared absorption band for the iminoacyl functionality is observed at 1567 cm^{-1}, 20 cm^{-1} lower than that for the *tert*-butyl analogue **191a**, suggesting that the C=N bond of the *tert*-butyl iminoacyl complex is significantly stronger than that in the cyclohexyl analogue. This suggests that these complexes may show different reactivities as confirmed by subsequent experiments. An analytically pure sample of complex **191b** was obtained as dark brownish-green cubes from a concentrated hexane solution at -35 °C.

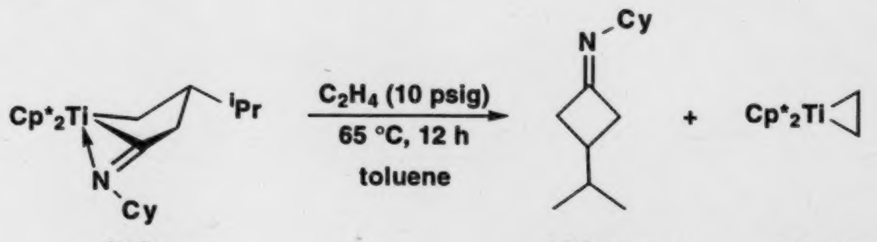
In fact, thermolysis of iminoacyl complexes **191a** and **191b** led to very interesting differences in reactivity. Heating a toluene solution of cyclohexyl η^2-iminoacyl complex **191b** affords the cyclohexylimine of 3-isopropylcyclobutanone **192** along with a small amount of the known pentamethylcyclopentadienyl (η^3: η^4-1,2,3-trimethyl-4,5-dimethylenecyclopentenyl) titanium complex **193** (Equation 3.4)[211]. However, thermolysis of complex **191b** in the presence of CO, ethylene, or diphenylacetylene does



(3.4)

191b **192** (72 %) **193** (5 %)

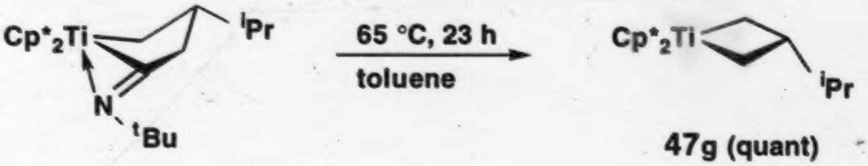
not lead to further insertion, in contrast to the observations of Whitby, for zirconacyclopentane complexes,[165,167,168,170] but instead gives only the cyclobutanone imine **192** (in higher yield) along with the corresponding permethyltitanocene ethylene adduct **194** (Equation 3.5). This reactivity is analogous to that observed for titanacyclopentane complexes.[164] Compound **192** is readily characterized by analysis of its spectroscopic data and comparison with previously reported compounds of the cyclobutanone imine class.[212]



(3.5)

191b **192** (94%) **194** (90%)

Surprisingly though, thermolysis of the *tert*-butyl analogue **191a** in the presence or absence of coordinating ligands under similar conditions leads to the efficient reformation of 3-isopropyl bis(pentamethylcyclopentadienyl)titanacylobutane **47g** by deinsertion of the isonitrile (Equation 3.6)! The ^{1}H NMR spectrum of the crude product mixture of this reaction shows no signals for the intact *tert*-butyl isonitrile, indicating that this deinsertion reaction probably occurs by a complex mechanism.



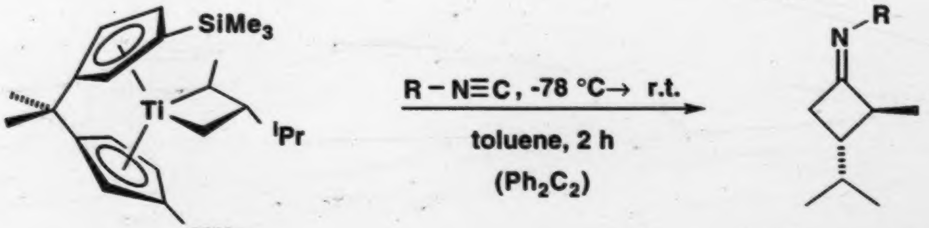
(3.6)

191a

47g (quant)

Despite the unsuccessful attempts to form CO insertion products with the *ansa*-bridged titanacyclobutane complexes, isonitrile insertion reactions were much more successful. Thus, treating 3-isopropyl-2-methyl titanacyclobutane complex **121a** with one equivalent of either cyclohexyl or *tert*-butyl isonitrile at low temperature affords cyclobutanimines **195a** and **195b** in high yield (Scheme 3.17). No tractable organometallic compound is observed, even in the presence of a trapping agent (carbon monoxide, ethylene, or diphenylacetylene) or by changing the stoichiometry to excess isonitrile. In contrast to the permethyltitanocene system, no intermediate iminoacyl complex is detected in these reactions.

Scheme 3.17



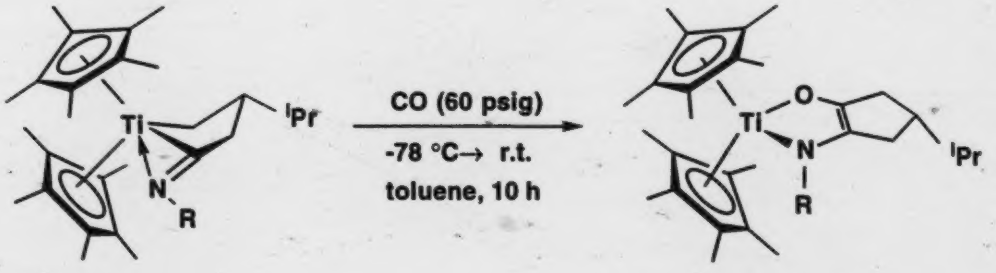
121a

	R
195a	^{t}Bu (80%)
195b	Cy (90%)

Assignment of the structure of **195b** follows from the analysis of the spectroscopic data. The α-methyl substituent is indicated by the three-hydrogen doublet at δ 1.23, while the presence of the isopropyl moiety is supported by two doublets at δ 0.77 and 0.75 for the diastereotopic methyl groups and a multiplet at δ 0.85 for the methine proton. The resonance for H-2 is observed as a multiplet at δ 2.63, which unfortunately overlaps with the signal for one of the α-methylene protons, while the resonance of H-3 is observed as a complex multiplet at δ 1.55. The resonance for the other α-methylene proton appears as at δ 2.04 (dd, J = 15.4, 7.5 Hz), while typical signals are observed for the cyclohexyl moiety. High resolution mass spectrometry of **195b** confirms its elemental composition. Structural assignment of *tert*-butyl imine **195a** was accomplished similarly.

The permethyltitanocene iminoacyl complexes **191a,b** undergo further ring expansion reactions by insertion of small organic compounds, enabling mixed insertion adducts to be synthesized. For example, subjecting the iminoacyl complexes to CO (60 psig) gives titanium amidoenolate complexes **196a,b** in very good yields (Scheme 3.18). Structural characterization of these complexes again follows from analysis of the spectroscopic data. For complex **196a**, the ^{1}H NMR spectrum shows resonances for four

Scheme 3.18



191a, 191b

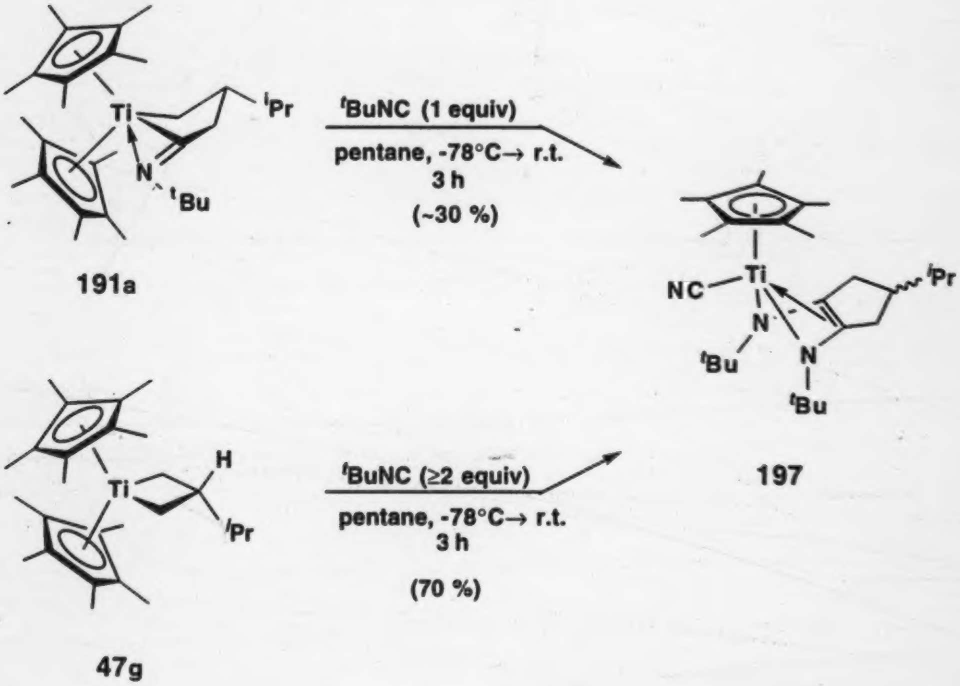
	R
196a	^{t}Bu (93 %)
196b	Cy (85 %)

inequivalent methylene protons as complex multiplets at δ 2.67, 2.49, 2.32 and 2.01, which along with a one-hydrogen multiplet at δ 1.61, define the cyclopentene ring. The expected resonances for the Cp*, isopropyl and *tert*-butyl groups are also observed. A gated decoupled ^{13}C NMR spectrum supports the structural assignment of **196a**. The quaternary vinylic carbon atoms of the cyclopentene ring are defined by the downfield singlet at δ 147.5 for the oxygen-bound carbon atom and 115.9 for the nitrogen-bound carbon atom. The triplets at δ 39.8 and 36.9 are assigned to the two allylic methylene carbon atoms, while the doublet at δ 34.2 is attributed to the methine carbon atom (C-3). The remaining signals in the spectrum are typical for inequivalent pentamethylcyclopentadienyl ligands. High resolution mass spectrometry confirms the elemental composition of complex **196a**. Analysis of the spectroscopic data of complex **196b** reveals its close structural similarity to complex **196a** and its structure has been assigned accordingly.

Further ring expansion of the iminoacyl complexes **191a** and **191b** with excess isonitrile was also investigated. Treatment of 2-*tert*-butylimino-4-isopropyl bis(pentamethylcyclopentadienyl)-titanacyclopentane **191a** with one equivalent of *tert*-butyl isonitrile at low temperature yields a dark green product in low yield. The same compound is formed when the 3-isopropyl bis(pentamethylcyclopentadienyl)-titanacyclobutane **47g** is treated with two equivalents of *tert*-butyl isonitrile under the same conditions. Although the isolated product appeared to contain the anticipated enediaminate moiety, other structural changes were also obvious.

Structural characterization of the product of this reaction is based on the analysis of spectroscopic and crystallographic data, revealing the product to be pentamethylcyclopentadienyl titaniumenediaminate complex **197** (Scheme 3.19). ^{1}H NMR analysis of this complex establishes the presence of two isomers, each having a single pentamethylcyclopentadienyl ligand (δ 1.89 and 1.29), equivalent isopropyl methyl groups (δ 0.91 and 0.89) and two equivalent *tert*-butyl groups (δ 1.91 and 1.26). In addition, the ^{13}C NMR spectrum showed singlets at δ 110.5 and 110.3, characteristic

Scheme 3.19


Ti
^{i}Pr
N
^{t}Bu
191a
^{t}BuNC (1 equiv)
pentane, -78°C→ r.t.
3 h
(~30 %)
Ti
H
^{i}Pr
47g
^{t}BuNC (≥2 equiv)
pentane, -78°C→ r.t.
3 h
(70 %)
NC
Ti
N
^{t}Bu
N
^{t}Bu
^{i}Pr
197

of quaternary vinylic nitrogen-substituted carbon atoms (*cf.* the amidoenolate complexes **196**), as well as two triplets (δ 35.3 and 33.6) and two doublets (δ 44.9 and 42.3). These ^{1}H and ^{13}C NMR resonances indicate the presence of the anticipated cyclopentenediaminate moiety. Additionally, however, the downfield ^{13}C NMR resonance at δ 156.1, along with a weak infrared absorption band at 2077 cm^{-1}, suggests the presence of the cyano moiety. Taken together, these spectroscopic data strongly suggest that this complex has a half-sandwich titanocene structure, with an inorganic cyanide ligand, as shown in Scheme 3.19. Confirmation of this structure was obtained by single crystal X-ray analysis of the *syn* isomer (Figure 3.1), which was obtained as diffractable single crystals by fractional crystallization from a hexane solution at -35 °C.

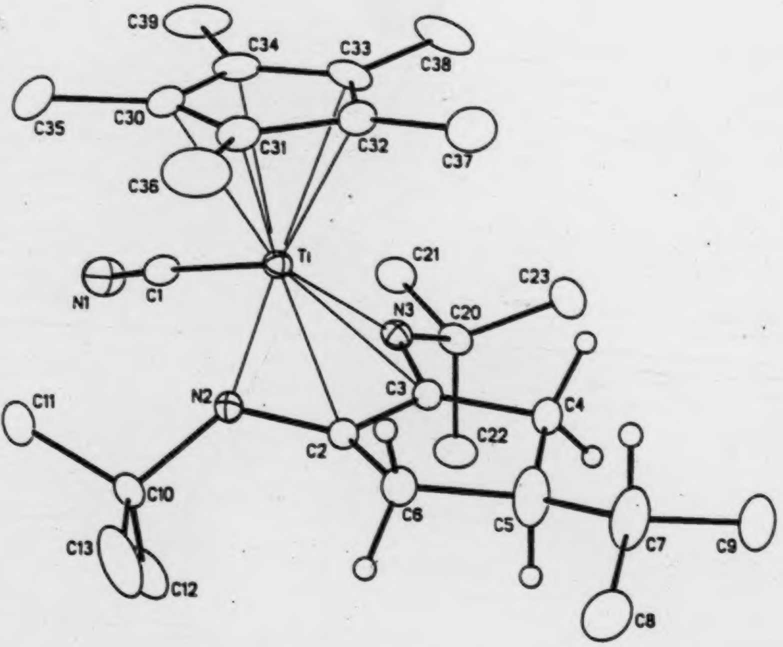

C39
C34
C33
C38
C35
C30
C31
C32
C37
C36
Ti
C21
C23
N1
C1
N3
C20
N2
C3
C4
C11
C2
C22
C10
C6
C5
C7
C9
C13
C12
C8

Figure 3.1. Perspective view of the [(η^5-C_5Me_5)Ti(CN)(η^4-1,2-{^{t}BuN}$_2$-4-^{i}Pr-C_5H_5)] **197** showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms attached to carbons C4, C5, C6 and C7 are shown with arbitrarily small thermal parameters, while methyl hydrogens (of the *t*-butyl, isopropyl and C_5Me_5 groups) are not shown.

This complex is both air-stable and extremely stable to heat, surviving prolonged treatment at 180 °C in a sealed NMR tube without change in isomeric ratio or observation of decomposition products. No change in the ^{1}H NMR spectrum of complex **197** is observed at temperatures down to -100 °C, indicating that each isomer has a static structure at room temperature. The cyclohexyl iminoacyl complex **191b**, unfortunately gave only complex product mixtures upon treatment with either cyclohexyl or *tert*-butyl isonitriles.

CONCLUSION

Regioselective addition of organic free radicals to the central carbon position of 1-substituted allyl titanocene complexes has been demonstrated, a reaction strongly dependent on the nature of the ancillary ligand. Crotyl and cinnamyl complexes with the one-atom *ansa*-[1]-titanocene templates, which provide more room in the wedge between the cyclopentadienyl rings, elicit central carbon alkylation reactivity provided weak donor substituents are attached to the cyclopentadienyl rings. Rather interestingly, only complexes with the *meso* stereochemistry mediate this reactivity; the corresponding *rac* analogues fail to yield central carbon alkylation products. It is likely that the *syn* orientation of the substituents in the *meso* template permits η^3-coordination of the crotyl and cinnamyl ligands without significant unfavorable steric interaction with the ancillary ligand. This is not the case for the *rac* analogues, presumably because the substituent on the η^3-crotyl or cinnamyl ligand suffers unfavorable steric interactions with the substituent on one of the cyclopentadienyl rings regardless of how the allylic fragment is oriented. Substituent effects in the *ansa*-bridged series also demonstrate clearly that minimum electron density at the metal center is a necessary requirement for radical addition to the central carbon position of substituted allyl complexes.

Perhaps most significantly, it was shown that aminotitanocene templates are very good substrates for central carbon alkylation of substituted allyl complexes. These results provide strong support for the hypothesis that delocalization of the nitrogen lone pair would significantly enhance the electron density at the metal center and facilitate $d \rightarrow \pi^*$ back bonding, in turn favoring η^3-coordination and promoting central carbon alkylation. On-going investigation in this area is focused on extending this alkylation reactivity to η^3-allyl complexes with alkoxy-substituted titanocene templates and developing intramolecular radical cyclization for applications to organic synthesis.

This investigation also revealed that samarium(II)-mediated radical alkylation of substituted allyl titanocene complexes is limited to reactions of non-stabilized organic radicals, failing with stabilized radicals such as benzyl and allyl radicals. However, this limitation can be circumvented by using photolytic decomposition of dialkylmercury compounds as a source of stabilized organic radicals, and suggests that other, more practical methodology for stabilized radical generation can be found.

This investigation has also demonstrated that controlled functionalization of titanacyclobutane complexes with small unsaturated molecules provides access to both four- and five-carbocyclic ring compounds. Controlled single insertion/reductive cyclization of carbon monoxide and alkyl isonitriles efficiently give cyclobutanones and cyclobutanimines, a new reaction demonstrated here for the first time. The double insertion of small molecules into the titanacyclobutane ring with subsequent demetallation, has been shown to give functionalized cyclopentanones and cyclopentenones. These results together demonstrate clearly the potential of this insertion/reductive cyclization strategy as a practical methodology for the synthesis of small carbocyclic ring compounds. Continuing work in this area is focused on extending the titanacyclobutane functionalization reactions to other substrates and other homologation strategies.

4 EXPERIMENTAL SECTION

Experimental procedures, spectroscopic and analytical data

General: All air-sensitive manipulations were conducted under a nitrogen atmosphere using standard Schlenk techniques or using a Vacuum Atmospheres He-553-2 Dri-lab equipped with a Mo-41-1 inert gas purifier, a CD-882 Dri-Cold Freezer maintained at -35 °C, and a DK-3E Dri-Kool mechanical refrigeration unit. Vacuum transfer of volatile reagents was performed at high vacuum (10^{-5} mm Hg) using MKS Baratron digital pressure transducers for measurement of gas pressure in known volume flasks. The high vacuum line was used to add solvent and volatile reagents to reaction mixtures at -196 °C via vacuum transfer and to remove volatile compounds from reaction mixtures. A Hanovia 450 watt high pressure mercury lamp was used in photolysis reactions, typically through a Pyrex filter at 0 °C.

Infrared (IR) spectra were recorded on Perkin-Elmer 1420, 298, and 283, Pye Unicam PU9522, and Nicolet 7199 Fourier transform spectrophotometers, and are reported in reciprocal wave numbers (cm^{-1}) calibrated to the 1601 cm^{-1} absorption of polystyrene. All infrared determinations were done on compounds applied as a film on KBr or KCl salt plates and are referred to as a "cast". The infrared absorption band (between 1480 and 1530 cm^{-1}) for the asymmetric C=C stretch of all allyl and crotyl complexes were assigned based on comparisons with literature values.[115,213] However, the corresponding assignment for the cinnamyl analogues was not possible due to the ambiguity in determining whether the absorption observed in this region of the IR spectrum was due to the phenyl or allyl moieties of the cinnamyl ligand. Nuclear magnetic resonance (NMR) spectra were recorded on Varian XL-300, Bruker AM-300 [300 MHz (^1H), 75 MHz (^{13}C)] and Bruker AM-400 [400 MHz (^1H) and 100 MHz (^{13}C)] spectrometers. Chemical shifts are reported in parts per million (ppm, δ) relative to TMS (^{1}H and ^{13}C) and coupling constants are reported in hertz (Hz). Unless stated otherwise, NMR spectra were obtained at 23 °C, and coupling constants reported as J refer to J_{HH} for ^{1}H NMR spectra and J_{CH} for ^{13}C NMR spectra or could not be unambiguously assigned due to the presence of multiple spin active atoms in close proximity. Coupling constants are reported to 0.1 hertz, which is within the limits of instrumental precision, but these values are normally accurate within ± 0.5 hertz. Multiplicities are reported as observed, *e.g.*, the α-methylene hydrogens of the titanacyclobutanes are observed as triplets (doublet of doublets with near identical coupling constants) and reported as such even though they arise from coupling between chemically different hydrogens. X-ray crystallographic analyses were done on a Siemans P4/RA X-ray diffractometer. Mass spectra were obtained on a Kratos MS-80 spectrometer operating at 40 eV. Combustion analyses were performed by the University of Alberta Microanalysis Laboratory. All air-sensitive compounds (~2.0 mg) were wrapped in strips of pre-weighed tin foil and kept in nitrogen-filled one-dram vials immediately prior to analysis. Abbreviations used in the assignment of metallacyclobutane resonances are "α" (positions adjacent to the metal) and "β" (position distal to the metal). The abbreviation "tuck" specifies the methylene of the η^5,η^1-$C_5Me_4CH_2$ ligand. The abbreviation "In" used in the NMR data for some titanacyclobutane complexes refers to an atom in the indenyl ligand. For the *ansa*-[1]-titanocene crotyl complexes, *meso* and *rac* refer to the relative spatial orientation of the two substituents on the cyclopentadienyl rings. *Meso* refers to complexes with the *syn*-cyclopentadienyl substituents, regardless of whether additional substituents or ligands render the complex, in fact, chiral, and *rac* refers to chiral complexes with *anti*-cyclopentadienyl substituents.

All carbonylation reactions above atmospheric pressure were done in a Lab Crest (Andrews Glass Co.) 3-ounce aerosol reaction vessel.[214] The yields of the volatile products from some carbonylation reactions were determined using a Hewlett-Packard 5890 Gas Chromatograph with infrared and flame ionization detectors using a HP5 column. These yields were quantified using peak areas for the corresponding compounds versus the peak area of 2-butanone introduced as a 0.069 M pentane solution. The conditions for chromatography include a split injection of the sample and a heating rate of 10 °C per minute.

Flash column chromatographic separations were performed on silica gel 60 (0.040-0.063 mm, E. Merck). Celite filtrations were performed using a plug of Hyflo Super Cel (Fisher) over glass wool in disposable pipets or alone on sintered glass funnels under vacuum. Cylindrical medium-walled Pyrex vessels equipped with Kontes k-826510 Teflon vacuum stopcocks are referred to as glass bombs.

Materials: Unless indicated otherwise, solvents and reagents were purchased from commercial vendors, distilled or passed down a plug of neutral alumina, and degassed prior to use by repeated freeze-pump-thaw cycles on a vacuum line. Benzene, hexanes, pentane, tetrahydrofuran, and diethyl ether were purified by distillation from sodium or potassium benzophenone ketyl. Dichloromethane was distilled from calcium hydride and deoxygenated prior to use.

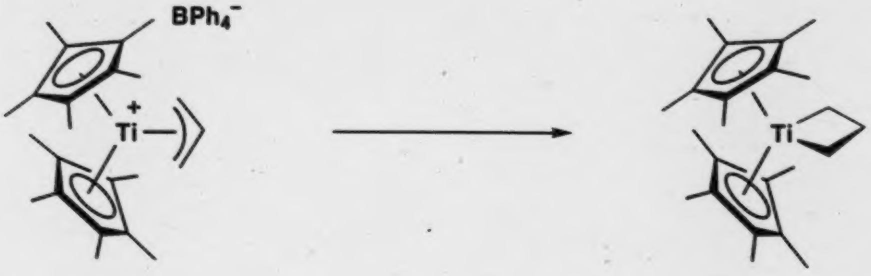
The following complexes were prepared according to published procedures: C_5Me_5H,[215] $Cp^*_2TiCl_2$ **50**,[84,216] $Cp^*_2Ti(\eta^3\text{-}C_3H_5)^+BPh_4^-$ **46**,[25] $Cp^*_2Ti(C_3H_5)$ **44**,[42] $[Cp'_2Fe]^+BPh_4^-$,[217] $Cp^*_2Ti(CH_3)_2$ **66**,[84,216] Cp_2Sm,[124] $Cp^*_2Ti(\eta^3\text{-}C_3H_4(C_6H_5))^+BPh_4^-$,[25] $Cp^*_2TiCH_2CH(R)CH_2$ (R = $CH_2C_6H_5$, C_3H_5, $CH(C_6H_5)_2$, $C_6H_5CH(CH_3)$) **47a,b,d,i**,[25,39,42] $Sm(HBpz^*_3)_2$ (pz* = 3,5-dimethylpyrazolyl),[120] $(CH_3)_2C(C_5H_5)_2$ **84**,[63] $(CH_3)_2Si(C_5H_5)_2$ **90**,[112,113] $(CH_3)_2Si(C_5H_4Si(CH_3)_3)_2$ **91**,[218] $(C_5H_4Si(CH_3)_3)_2TiCl$ **92**,[136] $[\eta^5\text{-}C_5H_3(1,3\text{-}SiMe_3)]_2TiCl$,[134] .

Benzylpotassium was prepared as previously described by Schlosser,[219] and 1-phenylethylpotassium and diphenylmethylpotassium were prepared analogously: addition of ^{n}BuLi to a slurry of KO^{t}Bu in the neat hydrocarbon at room temperature, isolation of the orange solid by filtration, followed by washing with benzene or toluene and drying *in vacuo*. Potassium enolates were prepared by addition of the ketone to a slurry of KH in hexanes, diethyl ether, or tetrahydrofuran, followed by filtration of the insoluble product through a sintered glass funnel under inert atmosphere. The product salt was then washed with hexanes, dried *in vacuo*, and used without further purification.

CHAPTER 2. CENTRAL CARBON ALKYLATION OF CATIONIC TITANIUM η^3-ALLYL COMPLEXES

2.1. Nucleophilic Addition to Cationic Titanium(IV) η^3-Allyl Complexes

Titanacyclobutane 47j from Allyl Complex 46:

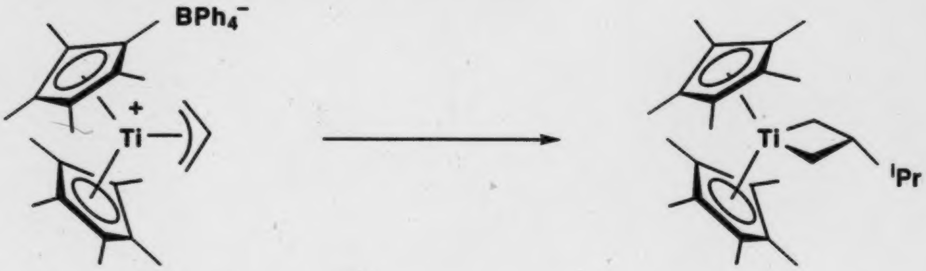


46

47j

Bis(pentamethylcyclopentadienyl)titanacyclobutane 47j. In the drybox, a Fischer-Porter bottle was charged with bis(pentamethylcyclopentadienyl)allyltitanium tetraphenylborate **46** (28.0 mg, 38 μmol) and THF (10 mL). The assembled apparatus was removed from the drybox, pressurized with ethylene (20 psi), and cooled to -78 °C. To this cooled solution was added 42 μL of lithium triethylborohydride *via* syringe (1 M in THF). The mixture was allowed to warm gradually to room temperature over a period of 12 h. The ethylene was released and the assembly taken into the drybox where THF was removed *in vacuo* from the resulting orange solution. The residue was triturated with pentane and filtered through celite. The filtrate was concentrated and subsequently cooled to -35 °C, yielding a red-brown crystalline solid (12.0 mg, 85%). Spectroscopic and high resolution mass spectrometry data for titanacyclobutane **47j**: ^{1}H NMR (200 MHz, C_6D_6): δ 1.81 (m, 4 H, α-CH_2), 1.66 (s, 30 H, $C_5(C\underline{H}_3)_5$), -0.15 (m, 1 H, β-CH_2). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, APT): δ 115.2 ($\underline{C}_5(CH_3)_5$), 73.6 (α-CH_2), 25.1 (β-CH_2), 11.7 ($C_5(\underline{C}H_3)_5$). IR (cm^{-1}, KBr, pentane cast): 2965 (s), 2907 (vs), 2858 (s), 1505 (m), 1439 (m), 1377 (vs), 1354 (m), 1257 (m), 1142 (m), 1075 (m), 1019 (m), 973 (m), 808 (s), 787 (s), 747 (s), 713 (s), 668 (m), 622 (m), 594 (w), 572 (w). MS Calcd for $C_{23}H_{36}Ti$ *m/e* 360.22964, found 360.22743.

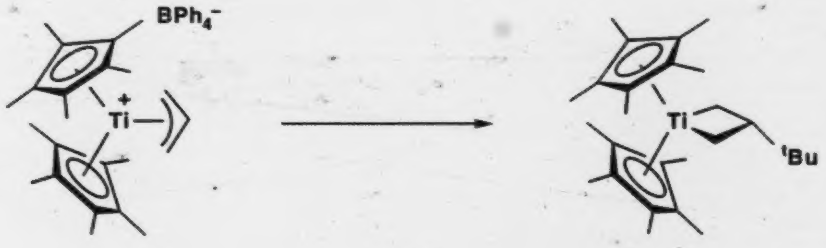
Isopropyl Titanacyclobutane 47g from Allyl Complex 46:



46 47g

Isopropyl bis(pentamethylcyclopentadienyl)titanacyclobutane 47g. A THF solution (10 mL) of bis(pentamethylcyclopentadienyl)allyltitanium tetraphenylborate **46** (150 mg, 0.221 mmol) in a Schlenk flask fitted with a rubber septum was cooled to -78 °C. Isopropylmagnesium chloride (111 µL, 2 M in ether) was added slowly *via* syringe. The reaction mixture was allowed to warm slowly to room temperature over a period of 6 h, during which time a color change from burgundy to bright red-orange occurred. The solvent was removed *in vacuo* and the red-orange residue triturated with pentane and filtered through a 1 inch layer of celite on a sintered-glass funnel. The filtrate was concentrated and subsequently cooled to -35 °C, yielding a red-brown crystalline solid (75.0 mg, 80%). Spectroscopic and analytical data for titanacyclobutane **47g**: ^1H NMR (400 MHz, C_6D_6): δ 1.76 (s, 15H, $C_5(CH_3)_5$), 1.63 (s, 15H, $C_5(CH_3)_5$), 1.18 (d, J = 6.3 Hz, 4H, α-CH); 1.02 (m, 1H, $C\underline{H}(CH_3)_2$), 0.86 (d, J = 8.0 Hz, 3H, $CH(C\underline{H}_3)_2$), 0.85 (d, J = 8.0 Hz, 3H, $CH(C\underline{H}_3)_2$), -0.95 (m, 1H, β-CH). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 117.8 (s, $\underline{C}_5(CH_3)_5$), 117.1 (s, $\underline{C}_5(CH_3)_5$), 71.5 (t, J = 133 Hz, α-CH_2), 34.8 (d, J = 126, $\underline{C}H(CH_3)_2$), 23.6 (q, J = 127, $CH(\underline{C}H_3)_2$); 22.3 (d, J = 134 Hz, β-CH), 12.3 (q, J = 125,1H)$C_5(\underline{C}H_3)_5$). IR (cm^{-1}, KBr, pentane cast): 2970 (vs), 2937 (vs), 2910 (vs), 2878 (s), 2856 (s), 1494 (m), 1457 (s), 1437 (s), 1376 (vs), 1354 (s), 1367 (w), 1266 (w), 1019 (s), 518 (m), 517 (m). Anal Calcd for C, 77.59; H, 10.52 ($C_{26}H_{42}Ti$). Found C, 77.33; H, 10.44.

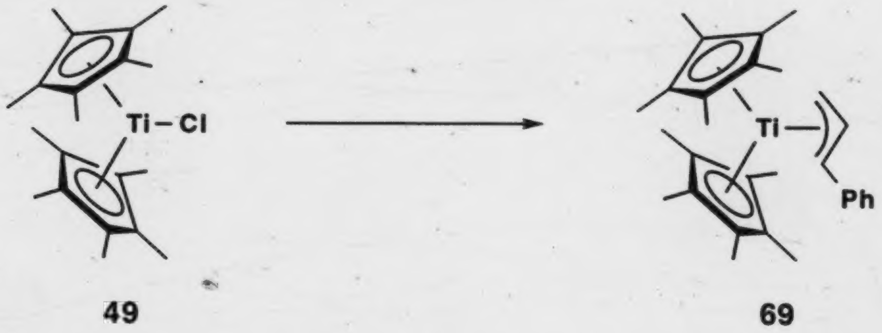
Titanacyclobutane 47e from Allyl Complex 46:



46 **47e**

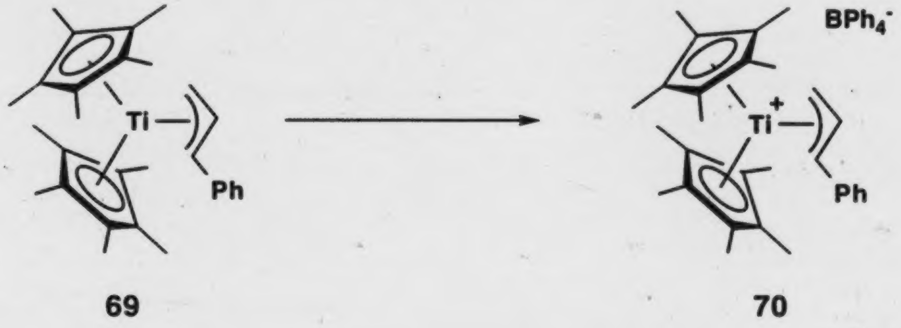
***tert*-Butyl bis(pentamethylcyclopentadienyl)titanacyclobutane 47e.**[25,39,42] A THF solution (10 mL) of bis(pentamethylcyclopentadienyl)titanium allyl tetraphenylborate (52.0 mg, 0.0738 mmol) in a Schlenk flask fitted with a rubber septum was cooled to -78 °C. *tert*-Butyl magnesium chloride (37 μL, 2 M in THF) was added slowly via syringe. The reaction mixture was allowed to warm slowly to room temperature over a period of 6 h, during which time the burgundy color of the reaction mixture changed to bright red-brown. The solvent was removed *in vacuo* and the resulting residue was triturated with pentane and filtered through a sintered-glass funnel containing 1 inch of celite. The red-brown filtrate was concentrated and cooled to -35 °C, yielding a red-brown solid (26.5 mg, 70%). Spectroscopic data for titanacyclobutane **47e**: ^1H NMR (400 MHz, C_6H_6): δ 1.79 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.65 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.06 (s, 9H, $C(C\underline{H}_3)_3$), 0.23 (complex multiplet, 4H, α-CH_2), -0.28 (m, 1H, β-CH). $^{13}C\{^1H\}$ (100.6 MHz, C_6D_6, APT): 119 ($\underline{C}_5(CH_3)_5$), 118.1 ($\underline{C}_5(CH_3)_5$); 61.6 (α-$\underline{C}H_2$), 35.1 ($\underline{C}(CH_3)_3$), 29.6 ($C(\underline{C}H_3)_3$); 27.8 (β-CH), 12.4 ($C_5(\underline{C}H_3)_5$), 11.4 ($C_5(\underline{C}H_3)_5$). IR (cm^{-1}, KBr, pentane cast): 2937 (vs), 2905 (vs), 2859 (vs), 1491 (m), 1474 (m), 1450 (s), 1435 (s), 1378 (vs, *tert*-butyl group), 1355 (m), 1215 (m), 1200 (m), 1064 (w), 1022 (s), 957 (w), 803 (w), 665 (w). Both elemental analysis and high resolution mass spectrometry failed despite several attempts.

Cinnamyl Complex 69 from Titanocene Chloride 49:



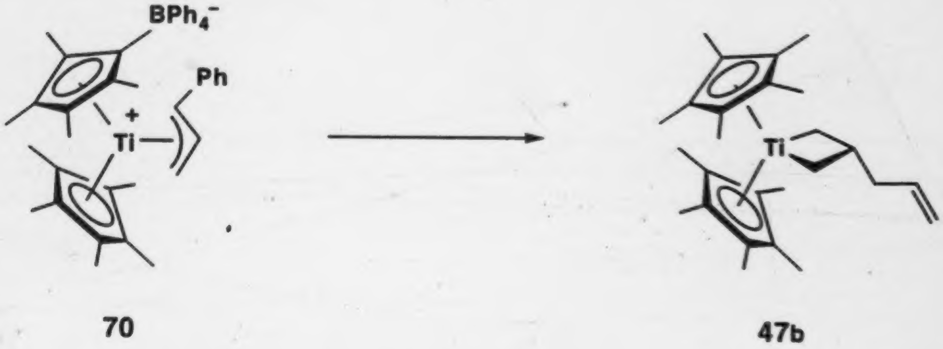
Bis(pentamethylcyclopentadienyl)titanium cinnamyl 69. In the drybox, to a THF solution (20 mL) of bis(pentamethylcyclopentadienyl)titanium chloride **49** (198 mg, 0.560 mmol) cooled to -35 °C was added a cooled (-35°C) THF solution of cinnamyllithium (70.0 mg, 0.560 mmol). After 10 minutes at this temperature, the reaction mixture was allowed to warm to room temperature and subsequently stirred for 1.5 h. Removal of the solvent *in vacuo* yielded a dark purple residue which was triturated with pentane and filtered through a sintered-glass funnel layered with celite. Concentration of the filtrate and cooling to -35 °C yielded dark purple cubes (209 mg, 86%). Spectroscopic (infrared only) data for cinnamyl complex **69**: IR (cm^{-1}, KBr, pentane cast): 2907 (vs), 2858 (s), 1594 (m), 1531 (m), 1492 (m), 1444 (m), 1378 (vs), 1257 (m), 1164 (m), 1070 (m), 1022 (m), 989 (m), 787 (s), 751 (m), 697 (s), 614 (m), 513 (m).

Cationic Cinnamyl Complex 70 from Cinnamyl Complex 69:



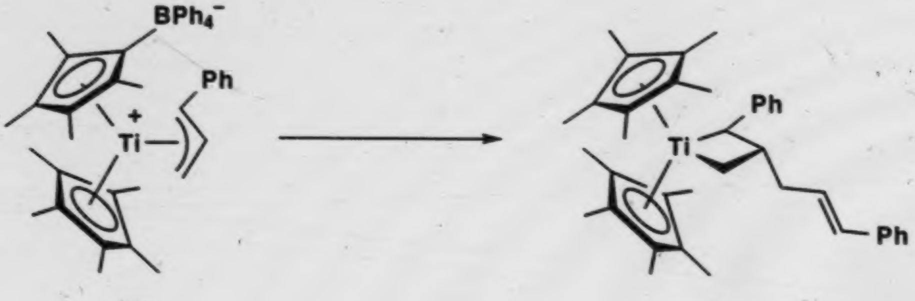
Bis(pentamethylcyclopentadienyl)titanium cinnamyl tetraphenylborate 70. In the drybox, a 50-mL round bottom flask was charged with $Cp^*_2Ti(C_3H_4Ph)$ **69** (0.51 g, 1.17 mmol) and $[Cp'_2Fe]^+BPh_4^-$ (0.62 g, 1.17 mmol). To the thoroughly mixed solids was added benzene (30 mL) at room temperature and the resulting mixture stirred for 3 h. An immediate precipitation of a burgundy colored solid occurred. Filtration through a sintered-glass funnel and washing with benzene (2 x 5 mL) yielded a burgundy solid (0.65 g, 73%), which was not further purified. Spectroscopic (^{1}H NMR only displaying $\eta^3 \rightarrow \eta^1$ isomerization as indicated by the increase in the number of one-hydrogen allyl multiplets) data for complex **70**: ^{1}H NMR (400.1 MHz, CD_2Cl_2, -100 °C): δ 7.55 (m, 25H), 6.44 (m, 1H), 6.32 (m), 6.15 (m), 5.08 (m, 1H), 5.06 (m, 1H), 4.16 (m, 1H), 3.45 (m), 1.99 (s, 30H).

Titanacyclobutane 47b from Cationic Cinnamyl Complex 70:



Allyl bis(pentamethylcyclopentadienyl)titanacyclobutane 47b.[39,42] A THF solution (10 mL) of bis(pentamethylcyclopentadienyl)titanium cinnamyl tetraphenylborate **70** (67.0 mg, 0.0881 mmol) in a Schlenk flask fitted with a rubber septum was cooled to -35 °C. Allylmagnesium chloride (44 μL, 2 M in THF) was added slowly via syringe. The reaction mixture was allowed to warm slowly to room temperature over a period of 6 h, during which time the burgundy color of the reaction mixture changed to bright red-brown. The solvent was removed *in vacuo* and the resulting residue was triturated with hexane and filtered through a sintered-glass funnel containing 1 inch of celite. Concentration of the filtrate and cooling to -35 °C yielded titanacyclobutane **47b** (12.0 mg, 30%).

Titanacyclobutane 74 from Cationic Cinnamyl Complex 70:



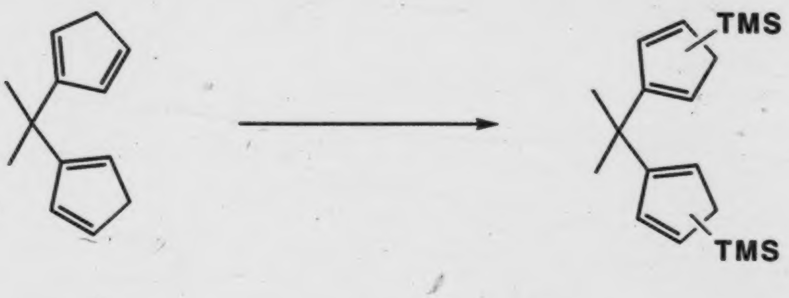
70

74

3-Cinnamyl-2-phenyl bis(pentamethylcyclopentadienyl)titanacyclobutane 74. A THF solution (10 mL) of bis(pentamethylcyclopentadienyl)titanium cinnamyl tetraphenylborate **70** (50.0 mg, 0.0663 mmol) in a Schlenk flask fitted with a rubber septum was cooled to -35 °C. Isopropylmagnesium chloride (33 µL, 2 M in THF) was added slowly via syringe. The reaction mixture was allowed to warm slowly to room temperature over a period of 6 h, during which time the burgundy color of the mixture changed to bright red-brown. The solvent was removed *in vacuo* and the resulting residue was triturated with hexane and filtered through a sintered-glass funnel containing 1 inch of celite. Concentration of the filtrate and cooling to -35 °C yielded titanacyclobutane **47b** (6.0 mg, 15%). Spectroscopic (partial ^{1}H NMR only) data of titanacyclobutane **74**: ^{1}H NMR (360.1 MHz, C_6D_6): δ 7.01 (m, 10H), 5.15 (m, 1H), 5.00 (m, 2H), 3.53 (m, 1H), 2.49 (t, J = 7.2 Hz, 1H, α-CH_2), 2.17 (m, 1H), 1.76 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.62 (s, 15H, $C_5(C\underline{H}_3)_5$), -0.33 (m, 1H, β-CH).

2.3.2. Synthesis of *ansa*-Bridged Titanium(III) η^3-Allyl Complexes

2,2-Bis(3'-trimethylsilylcyclopentadienyl)propane 86 from Compound 85:



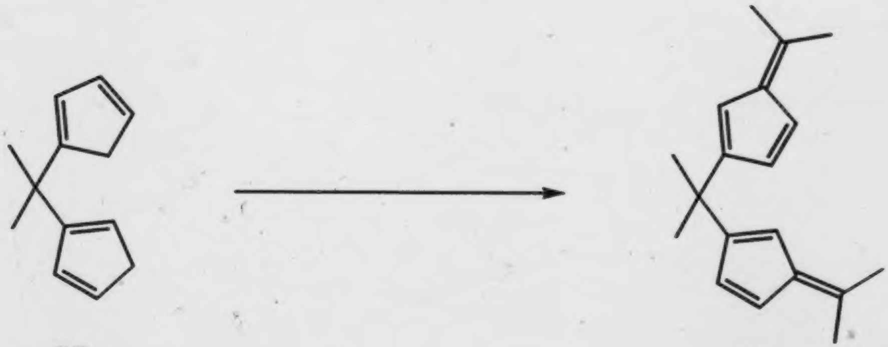
85 **86**

2,2-Bis(3'-trimethylsilylcyclopentadienyl)propane 86. In a Schlenk flask, a THF solution of the dilithium salt of 2,2-bis(cyclopentadienyl)propane[63] **85** (7.15 g, 0.0388 mol) cooled to -78 °C. Chlorotrimethylsilane (10.1 mL, 0.0777 mol) was slowly added to this cooled solution. The reaction mixture was allowed to warm to room temperature (overnight), after which time the mixture was quenched and the organic layer washed with water (5 x 20 mL) until the aqueous extract was neutral to pH paper. The organic layer was dried with anhydrous $MgSO_4$ and the solvent removed *in vacuo* to yield **86** (6.52 g, 53%) as a mixture of inseparable equilibrating double bond isomers. Spectroscopic (^{1}H NMR only) and mass spectrometry data for compound **86**: ^{1}H NMR: (300 MHz, $CDCl_3$): 6.45 (m, 1H), 6.35 (m, 1H), 6.1 (m, 2H), 1.45 (s, 6H, $C(C\underline{H}_3)_2$), 1.40 (m, 4H), -0.03 (s, 18H, $Si(C\underline{H}_3)_3$). MS Calcd for $C_{19}H_{32}Si_2$ *m/e* Found (low resolution MS) M$^+$ 316.0 (14%); 242.8 (8%); 178.9 (23%); 122.2 (12%); 73.1 (100%).

Dilithium salt of 2,2-bis(3'-trimethylsilylcyclopentadienyl)propane. *n*Butyllithium (10.0 mL 1.6 M in hexanes) was added to a cooled (-78 °C) diethyl ether solution of 2,2-bis(3'-trimethylsilylcyclopentadienyl)propane (2.10 g, 0.0266 mmol) in a Schlenk flask.

The reaction mixture was allowed to warm to room temperature and subsequently stirred for 6 h. Removal of the solvent *in vacuo* yielded a cream-colored residue which was washed with hexane (3 x 20 mL) to give an off-white powder (1.116 g, 52%). This material was used without further characterization.

Fulvene 87 from 2,2-bis(cyclopentadienyl)propane 85:

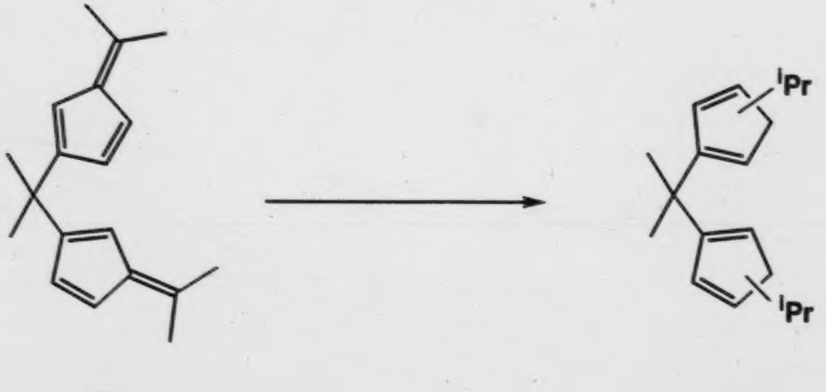


85 **87**

Fulvene 87. Acetone (0.70 mL, 9.87 mmol) and 2,2-bis(cyclopentadienyl)propane **85** (0.85 g, 4.93 mmol) were added to a mixture of methanol and diethyl ether (12 mL of a 10 : 1 mixture) in a 50 mL round bottom flask. Pyrrolidine (2.0 mL, 0.0296 mol) was added to this solution and the reaction mixture stirred for 17 h at room temperature. The reaction mixture darkened during this time. The mixture was neutralized with glacial acetic acid (10 mL) followed by the addition of water (15 mL). Extraction of this mixture with 5 x 20 mL diethyl ether / pentane (1 : 1) yielded a fluorescent greenish-yellow solution which was washed with water (2 x 20 mL) and subsequently dried over anhydrous magnesium sulfate. Filtration and removal of the solvents gave a fluorescent greenish-yellow oil (1.04 g, 84%). Spectroscopic (^{1}H NMR only) and high resolution mass spectrometry data for compound **87**: ^{1}H NMR (300.1 MHz, $CDCl_3$) δ 6.49 (dd, J =

5.2, 2.2 Hz, 2H), 6.42 (dd, *J* = 5.2, 1.5 Hz, 2H), 6.22 (t, *J* = 1.9 Hz, 2H), 2.17 (s, 6H), 2.16 (s, 6H), 1.49 (s, 6H). MS Calcd for $C_{19}H_{24}$, *m/e* 252.18781, found 252.18766.

2,2-Bis(3'-isopropylcyclopentadienyl)propane 88 from Fulvene 87:

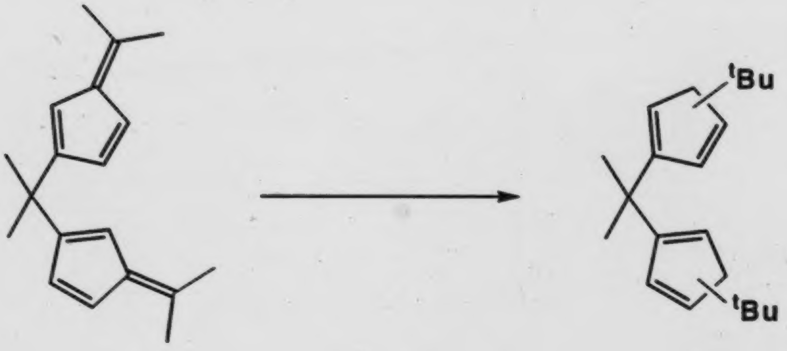


87 **88**

2,2-Bis(3'-isopropylcyclopentadienyl)propane 88. A diethyl ether solution of compound **87** (1.10 g, 4.358 mmol) in a Schlenk flask was slowly added (*via* cannula) to a stirred diethyl ether suspension of lithium aluminum hydride (0.310 g, 4.36 mmol) in a second Schlenk flask at room temperature. The mixture was stirred for 4 h and then quenched with water.[220] The diethyl ether layer was separated and washed with water (3 x 10 mL), then with saturated NaCl solution and subsequently dried over anhydrous $MgSO_4$. Removal of the solvent *in vacuo* yielded compound **88** as a pale yellow oil (0.58 g 52%), which is a mixture of inseparable equilibrating isomeric compounds. Spectroscopic (^{1}H NMR only) and high resolution mass spectrometry data for compound **88**: ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 6.02 m, 2.89 m, 2.82 m, 2.55 m, 1.41 m, 1.14 m. MS Calcd for $C_{19}H_{28}$ *m/e* 256.21912, found 256.21836.

Dilithium salt of 2,2-bis(3'-isopropylcyclopentadienyl)propane. To a cooled (-78 °C) pentane solution of 2,2-bis(3'-isopropylcyclopentadienyl)propane **88** (1.20 g, 4.68 mmol) in a 50 mL Schlenk flask was added nBuLi (5.9 mL 1.6 M in hexanes) *via* syringe. The reaction mixture was stirred at this temperature for 0.5 h and then allowed to warm to room temperature. After 3 h at room temperature, the pentane was removed *in vacuo* and the whitish residue was taken into the drybox and washed with pentane (3 x 20 mL), yielding a white solid (1.052 g, 84%). This material was used without further characterization.

2,2-Bis(3'-*tert*-butylcyclopentadienyl)propane 89 from Fulvene 87:

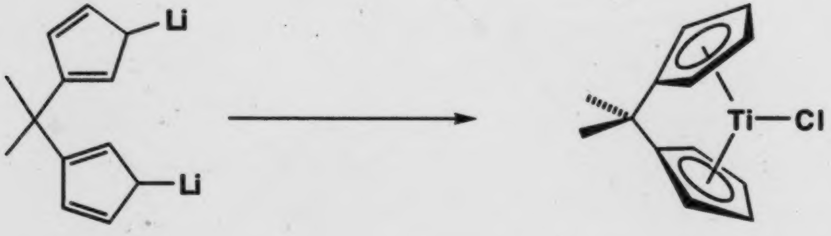


87 **89**

2,2-Bis(3'-*tert*-butylcyclopentadienyl)propane 89. To a cooled (-78 °C) diethyl ether solution of compound **87** (0.78 g, 3.09 mmol) in a Schlenk flask was added 3 equivalents of methyllithium (6.6 mL, 1.4 M in diethyl ether). The reaction mixture was stirred overnight after which it was quenched with water and the layers separated. The ether layer was washed three times with water, once with saturated NaCl solution, and subsequently dried over anhydrous $MgSO_4$. Removal of the solvent *in vacuo* yielded a pale yellow oil (0.78 g, 89%).

Dilithium salt of 2,2-bis(3'-*tert*butylcyclopentadienyl)propane. To a cooled (-78 °C) pentane solution of 2,2-bis(3'-isopropylcyclopentadienyl)propane **89** (0.78 g, 2.74 mmol) in a 25 mL Schlenk flask was added nBuLi (3.5 mL 1.6 M in hexanes) *via* syringe. The reaction mixture was stirred at this temperature for 0.5 h and then allowed to warm to room temperature. After 3 h at room temperature, the pentane was removed *in vacuo* and the whitish residue was taken into the drybox and washed with pentane (3 x 10 mL), yielding a white solid (0.8 g, quant.). This material was used without further characterization.

***ansa*-[1]-Titanocene Chloride 92 from Dilithium salt of Compound 85**:

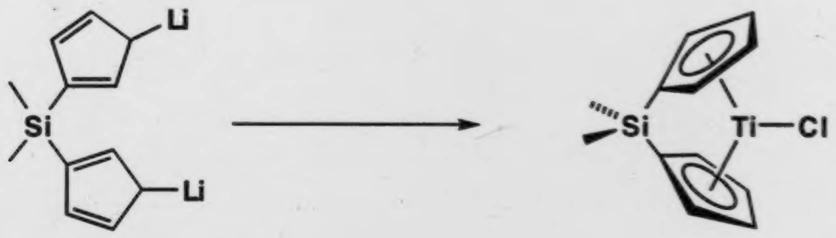


85-Li$_2$

92

***ansa*-[1]-{Dimethylmethano bis(cyclopentadienyl)}titanium chloride 92**. In the drybox, a THF solution (5 mL) of the dilithium salt of 2,2-bis(cyclopentadienyl)propane[63] (107 mg, 0.581 mmol) and a THF suspension of $TiCl_3$•3THF (209 mg, 0.564 mmol) was cooled to -35 °C for 0.5 h. The solution of the dilithium salt was added slowly to the $TiCl_3$•3THF suspension and the reaction mixture allowed to warm gradually to room temperature over a period of 12 h and subsequently stirred for an additional 6 h at room temperature. The solvent was removed *in vacuo* and the pinkish-brown residue was extracted several times with pentane. The combined extracts were filtered through a sintered-glass funnel layered with about 1 inch of celite. The filtrate was concentrated and subsequently cooled to -35 °C, yielding a pinkish-brown solid (140 mg, 90%). This paramagnetic product was characterized by high resolution mass spectrometry: MS Calcd for $C_{13}H_{14}TiCl$, *m/e* 253.02635, found 253.02247.

ansa-[1]-Titanocene Chloride 93 from Dilithium salt of Compound 90:

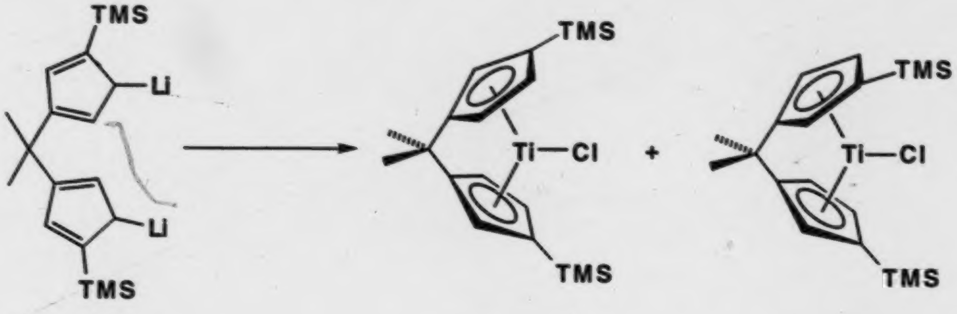


90-Li$_2$ **93**

ansa-[1]-{Dimethylsilyl bis(cyclopentadienyl)}titanium chloride 93.[122] In a Schlenk flask, a mixture of the dilithium salt of 2,2-bis(cyclopentadienyl)silane[112,113] (2.35 g, 0.0116 mol) and crystalline $TiCl_3$•3THF (4.31 g, 0.0116 mol) was cooled to -78°C. Cooled THF (100 mL) was added *via* cannula to the solid mixture. The resulting reaction mixture was allowed to warm to room temperature over a period of 12 h and subsequently stirred for an additional 6 h at room temperature. The solvent was removed *in vacuo* and the resulting dark red residue was extracted with benzene (4 x 10 mL). The combined extracts were filtered through a sintered-glass funnel layered with celite. Removal of the benzene from the filtrate yielded a pinkish-brown solid (2.8 g, 90%).

$PbCl_2$ oxidation (0.5 equivalent $PbCl_2$ in THF at room temperature for 3 h) of a sample of this material yielded the known dichloride complex **113**.[112,122]

***meso* and *rac ansa*-[1]-Titanocene Chloride 94 from Dilithium salt of Compound 86**:



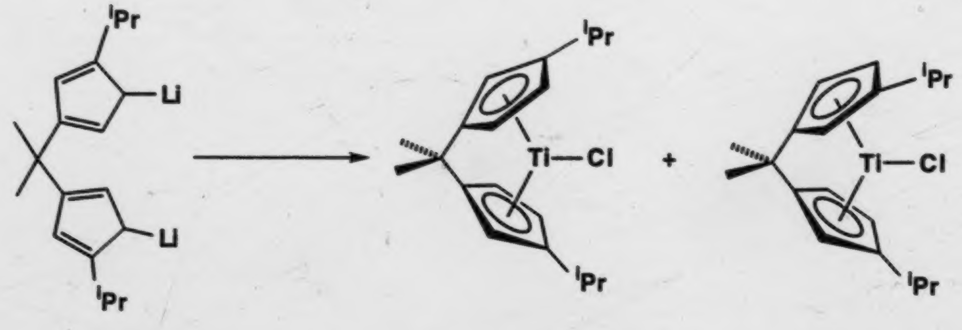
86-Li_2 **94-*rac*** **94-*meso***

***Meso* and *rac ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}-titanium chloride 94**. The dilithium salt of 2,2-bis(3'-trimethylsilylcyclopentadienyl)propane **86** (5.69 g, 0.01731 mol) and $TiCl_3$•3THF (6.42 g, 0.0173 mol) were mixed together in a 200 mL Schlenk flask and cooled to -78 °C. 100 mL of cooled THF (-78 °C) was transferred by cannula onto the solids and the reaction mixture was allowed to warm to room temperature overnight. The solvent was removed *in vacuo* and the resulting dark brown residue was extracted with pentane (5 x 10 mL) and the solution filtered through a sintered-glass funnel layered with celite. The filtrate was concentrated and cooled to -35 °C, yielding the *meso* isomer. Concentrating and cooling was repeated several times to maximize the yield of the *meso* isomer (778.4 mg, 11%). The *rac* isomer was subsequently obtained from the mother liquor cooled to -35 °C (405 mg, 5.7%). The ratio of *meso* to *rac* isomer was determined to be 1 : 2.6 by ^1H NMR analysis of the dichloride complexes formed by $PbCl_2$ oxidation (0.5 equivalent $PbCl_2$ in

THF at room temperature for 1 h) of a crude mixture of the monochloride complexes, assuming no *rac/meso* isomerization occurs during that process. The paramagnetic monochloride complexes were characterized by high resolution mass spectrometry as a mixture: MS Calcd *m/e* 397.10541 ($C_{19}H_{30}TiSi_2$), found 397.10604.

***Meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium dichloride.** ^1H NMR (400.1 MHz, $CDCl_3$): δ 6.99 (t, *J* = 2.3 Hz, 2H), 5.39 (t, *J* = 2.3 Hz, 2H), 5.29 (t, *J* = 2.3 Hz, 2H), 1.25 (s, 3H, $C(C\underline{H}_3)_2$), 0.99 (s, 3H, $C(C\underline{H}_3)_2$), 0.46 (s, 18H, $Si(C\underline{H}_3)_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, APT): δ 139.7 ($C_{methine}$), 139.4 ($C_{quaternary}$), 117.5 ($C_{methine}$), 116.4 ($C_{quaternary}$), 113.1 ($C_{methine}$), 36.9 ($\underline{C}(CH_3)_2$), 25.1 ($C(\underline{C}H_3)_2$), 22.5 ($C(\underline{C}H_3)_2$), -0.6 ($Si(\underline{C}H_3)_3$). MS Calcd for $C_{19}H_{30}TiSi_2Cl_2$ *m/e* 432.07425, found 432.07497. ***Rac ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium dichloride.** ^1H NMR (400.1 MHz, $CDCl_3$): δ 6.98 (t, *J* = 2.6 Hz, 2H), 5.32 (t, *J* = 2.6 Hz, 2H), 5.25 (t, *J* = 2.6 Hz, 2H), 1.15 (s, 6H, $C(C\underline{H}_3)_2$), 0.42 (s, 18H, $Si(C\underline{H}_3)_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, APT): δ 140.4 ($C_{quaternary}$), 139.2 ($C_{methine}$), 117.6 ($C_{quaternary}$), 114.8 ($C_{methine}$), 113.9 ($C_{methine}$), 36.5 ($\underline{C}(CH_3)_2$), 23.3 ($C(\underline{C}H_3)_2$), -0.6 ($Si(\underline{C}H_3)_3$). $C_{19}H_{30}TiSi_2Cl_2$ *m/e* 432.07425, found 432.07358.

***Meso* and *rac ansa*-[1]-Titanocene Chloride 95 from Dilithium salt of Compound 88:**

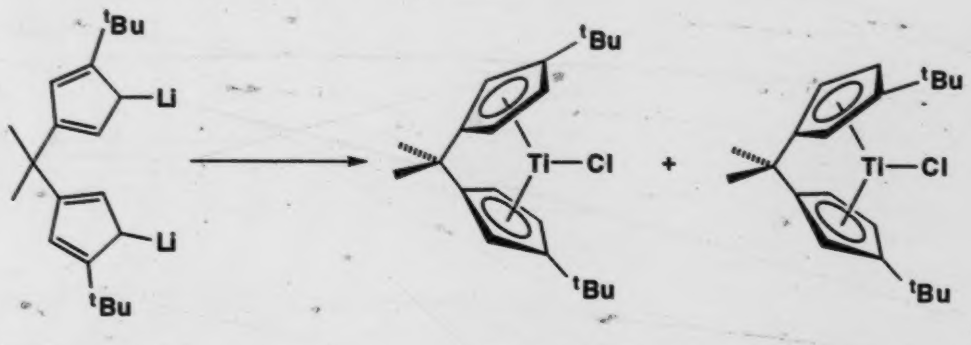


88-Li$_2$ **95-*rac*** **95-*meso***

***Meso* and *rac ansa*-[1]-{dimethylmethano bis(3-isopropylcyclopentadienyl)}titanium chloride 95.** The dilithium salt of 2,2-bis(3'-isopropylcyclopentadienyl)propane **88** (1.052 g, 3.92 mmol) and $TiCl_3$•3THF (1.45 g, 3.92 mmol) were mixed together in a 100 mL Schlenk flask and cooled to -78 °C. 50 mL of cooled THF (-78 °C) was transferred by cannula onto the solids and the reaction mixture was allowed to warm to room temperature overnight. The solvent was removed *in vacuo* and the resulting dark brown residue was extracted with pentane (5 x 10 mL) and the solution filtered through a sintered-glass funnel layered with celite. The filtrate was concentrated and cooled to -35 °C, yielding the *meso* isomer. Concentrating and cooling was repeated several times to maximize the yield of the *meso* isomer (193 mg, 14.6%). The *rac* isomer was obtained from the mother liquor cooled to -35 °C (104.1 mg, 7.9%). The ratio of *meso* to *rac* isomer was determined to be 1 : 1 by ^1H NMR analysis of the dichloride complex formed by $PbCl_2$ oxidation (0.5 equivalent $PbCl_2$ in THF at room temperature for 1 h) of a crude mixture of the monochloride complexes, assuming no *rac/meso* isomerization occurs during that process. The paramagnetic monochloride complexes were characterized by high resolution mass spectrometry as a mixture: MS Calcd $C_{19}H_{26}TiCl$ *m/e* 337.12024 found 337.12008.

***Meso ansa*-[1]-{dimethylmethano bis(3-isopropylcyclopentadienyl)}titanium dichloride.** ^1H NMR (300.1 MHz, $CDCl_3$): δ 6.58 (t, *J* = 3.0 Hz, 2H), 5.65 (t, *J* = 3.0 Hz, 2H), 4.97 (t, *J* = 3.0 Hz, 2H), 3.21 (septet, *J* = 6.9, 1H, $C\underline{H}(CH_3)_2$), 1.84 (s, 3H, $C(C\underline{H}_3)_2$), 1.66 (s, 3H, $C(C\underline{H}_3)_2$), 1.34 (d, *J* = 6.9 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.14 (d, *J* = 6.9 Hz, 6H, $CH(C\underline{H}_3)_2$). ***Rac ansa*-[1]-{dimethylmethano bis(3-isopropylcyclopentadienyl)}titanium dichloride.** ^1H NMR (300.1 MHz, $CDCl_3$): δ 6.70 (t, *J* = 3.0 Hz, 2H), 5.38 (t, *J* = 3.0 Hz, 2H), 5.17 (t, *J* = 3.0 Hz, 2H), 3.11 (septet, *J* = 6.9, 1H, $C\underline{H}(CH_3)_2$), 1.75 (s, 6H, $C(C\underline{H}_3)_2$), 1.32 (d, *J* = 6.9 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.14 (d, *J* = 6.9 Hz, 6H, $CH(C\underline{H}_3)_2$).

***Rac ansa*-[1]-Titanocene Chloride 96 from Dilithium salt of Compound 89**:

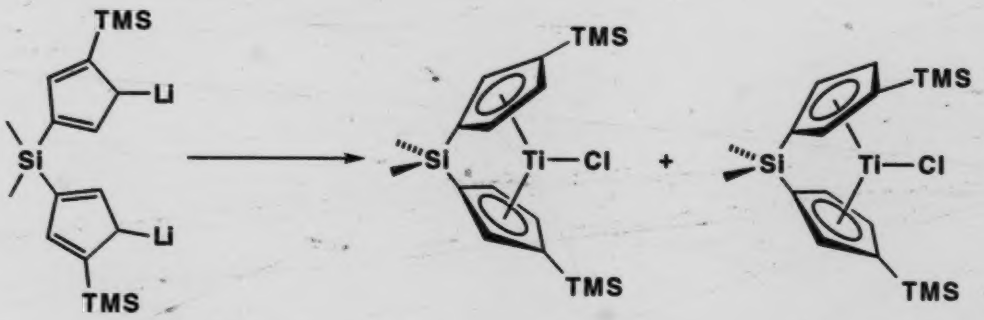


89-Li$_2$ **96-*rac*** **96-*meso***

***Meso* and *rac ansa*-[1]-{dimethylmethano bis(3-*tert*-butylcyclopentadienyl)}titanium chloride 96**. The dilithium salt of 2,2-bis(3'-*tert*-butylcyclopentadienyl)propane **89** (167 mg, 0.564 mmol) and $TiCl_3 \cdot 3THF$ (209 mg, 0.564 mmol) were mixed together in a 50 mL Schlenk flask and cooled to -78 °C. 25 mL of cooled THF (-78 °C) was transferred by cannula onto the solids and the reaction mixture was allowed to warm to room temperature overnight. The solvent was removed *in vacuo* and the resulting dark brown residue was extracted with pentane (4 x 10 mL) and the solution filtered through a sintered-glass funnel layered with celite. The filtrate was concentrated and cooled to -35 °C, giving the *rac* isomer only (82.0 mg, 40%). ^{1}H NMR analysis of the dichloride complex formed by $PbCl_2$ oxidation (0.5 equivalent $PbCl_2$ in THF at room temperature for 1 h) of a crude mixture of the monochloride complex, assuming no *rac/meso* isomerization occurs during that process, determined that the *rac* isomer was formed selectively. The paramagnetic product was characterized by high resolution mass spectrometry: MS Calcd for $C_{21}H_{30}TiCl$, *m/e* 365.15155, found 365.15122.

***Rac ansa*-[1]-{dimethylmethano bis(3-*tert*-butylcyclopentadienyl)}titanium dichloride**. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 6.72 (t, *J* = 3.0 Hz, 2H), 5.16 (t, *J* = 3.0 Hz, 2H), 5.11 (t, *J* = 3.0 Hz, 2H), 1.42 (s, 18H, C($C\underline{H}_3$)$_3$), 1.10 (s, 9H, Si($C\underline{H}_3$)$_3$).

***Meso*- and *rac*- Titanocene Chloride 97 from Compound 91:**

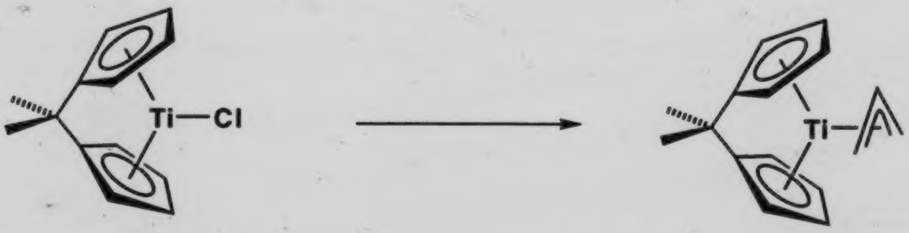


91-Li$_2$ **97-*rac*** **97-*meso***

***Meso* and *rac ansa*-[1]-{dimethylsilyl bis(3-trimethylsilylcyclopentadienyl)}titanium chloride 97.** The dilithium salt of 2,2-bis(3'-trimethylsilylcyclopentadienyl)silane **91**[218] (4.01 g, 0.012 mol) and $TiCl_3$•3THF (4.32 g, 0.012 mol) were mixed together in a 200 mL Schlenk flask and cooled to -78 °C. 100 mL cooled THF (-78 °C) was transferred by cannula onto the solids and the reaction mixture was allowed to warm to room temperature overnight. The solvent was removed *in vacuo* and the resulting dark brown residue was extracted with pentane (5 x 10 mL) and the solution filtered through a sintered-glass funnel layered with celite. The filtrate was concentrated and cooled to -35 °C, yielding the *meso* isomer. Concentrating and cooling was repeated several times to maximize the yield of the *meso* isomer (500 mg, 10%). The *rac* isomer remaining in the mother liquor was not isolated due to considerable amounts of pentane-soluble impurities. The ratio of *meso* to *rac* isomer was determined to be 1 : 1 by ^{1}H NMR analysis of the dichloride complex formed by $PbCl_2$ oxidation (0.5 equivalent $PbCl_2$ in THF at room temperature for 1 h) of a crude mixture of the monochloride complexes, assuming no *rac/meso* isomerization occurs during that process. The paramagnetic monochloride product was characterized by high resolution mass spectrometry: MS Calcd $C_{18}H_{30}TiSi_3Cl$, *m/e* 413.08234, found 413.07996.

***Meso ansa*-[1]-{dimethylsilyl bis(3-trimethylsilylcyclopentadienyl)}titanium dichloride.** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.26 (t, *J* = 2.4 Hz, 2H), 6.23 (t, *J* = 2.4 Hz, 2H), 6.07 (t, *J* = 2.4 Hz, 2H), 0.79 (s, 3H, $Si(C\underline{H}_3)_2$), 0.58 (s, 3H, $Si(C\underline{H}_3)_2$), 0.32 (s, 18H, $Si(C\underline{H}_3)_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, APT): δ 146.6 ($C_{methine}$), 139.6 ($C_{quaternary}$), 131.7 ($C_{methine}$), 116.6 ($C_{methine}$), 105.8 ($C_{quaternary}$), -0.1 ($Si(\underline{C}H_3)_3$), -3.1 ($Si(\underline{C}H_3)_2$), -6.9 ($Si(\underline{C}H_3)_2$). ***Rac ansa*-[1]-{dimethylsilyl bis(3-trimethylsilylcyclopentadienyl)}titanium dichloride.** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.11 (t, *J* = 2.6 Hz, 2H), 6.19 (t, *J* = 2.6 Hz, 2H), 6.08 (t, *J* = 2.6 Hz, 2H), 0.71 (s, 6H, $Si(C\underline{H}_3)_2$), 0.28 (s, 18H, $Si(C\underline{H}_3)_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, APT): δ 140.4 ($C_{quaternary}$), 139.2 ($C_{methine}$), 117.6 ($C_{quaternary}$), 114.8 ($C_{methine}$), 113.9 ($C_{methine}$), 36.5 ($\underline{C}(CH_3)_2$), 23.3 ($C(\underline{C}H_3)_2$), -0.6 ($Si(\underline{C}H_3)_3$).

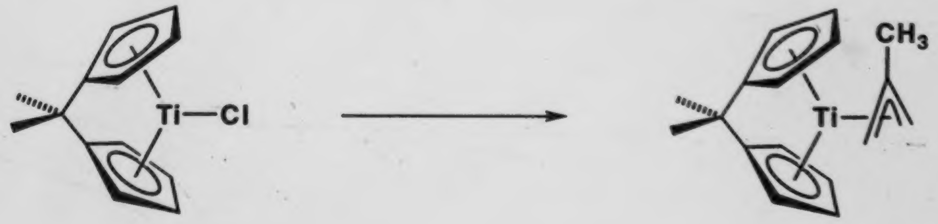
***ansa*-[1]-Titanocene Allyl 98 from Titanocene Chloride 92:**



92 **98**

***ansa*-[1]-{Dimethylmethano bis(cyclopentadienyl)}titanium allyl 98.** In the drybox, a 50 mL round bottom flask containing *ansa*-[1]-{dimethylmethano bis(cyclopentadienyl)}titanium chloride **92** (1.09 g, 2.16 mmol) in toluene (20 mL) was cooled to -35 °C. Allylmagnesium chloride (2.5 mL, 2 M in THF) was then added by syringe to the cooled solution and after 10 minutes at -35 °C, the reaction mixture was allowed to warm to room temperature and stirred for 1.5 h. The solvents were removed *in vacuo* and the resulting dark purple residue was triturated with pentane and the solution filtered through a sintered-glass funnel layered with celite. The filtrate was concentrated and cooled to -35 °C, yielding complex **98** as purple micro-needles (416 mg, 37%). This air-sensitive paramagnetic complex was characterized by infrared spectroscopy and elemental analysis: IR (cm^{-1}, KBr, cast): 3068 (m), 2978 (vs), 2962 (vs), 2930 (vs), 2897 (vs), 1598 (m), 1547 (s), 1506 (vs, η^3-allyl),[115,213] 1468 (s), 1451 (s), 1421 (s), 1380 (s), 1367 (m), 1272 (s), 1248 (s), 1041 (vs), 1026 (vs, Cp), 911 (m), 875 (m), 795 (vs), 731 (m). Anal Calcd $C_{16}H_{19}Ti$: C, 74.14; H, 7.39. Found for C, 74.27; H, 7.57.

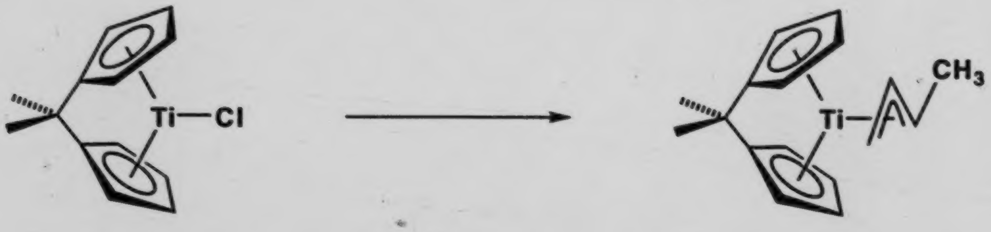
***ansa*-[1]-Titanocene 2-Methylallyl 99 from Titanocene Chloride 92:**



92 **99**

***ansa*-[1]-{Dimethylmethano bis(cyclopentadienyl)}titanium 2-methylallyl 99.** In the drybox, a 50 mL round bottom flask containing *ansa*-[1]-{dimethylmethano bis(cyclopentadienyl)}titanium chloride **92** (0.550 g, 1.084 mmol) in toluene (20 mL) was cooled to -35 °C. 2-Methylallylmagnesium chloride (1.8 mL, 1.35 M in THF) was then added via syringe to the cooled solution and after 10 minutes at -35 °C, the reaction mixture was allowed to warm to room temperature and stirred for 1.5 h. The solvents were removed *in vacuo* and the resulting dark purple residue was triturated with pentane and the solution filtered through a sintered-glass funnel layered with celite. The filtrate was concentrated and cooled to -35 °C, yielding complex **99** as purple micro-needles (140 mg, 24%). This air-sensitive paramagnetic complex was characterized by infrared spectroscopy and elemental analysis: IR (cm^{-1}, KBr, cast): 2918 (m), 2978 (m), 2964 (m), 1598 (m), 1489 (m, η^3-allyl),[115,213] 1469 (m), 1455 (m), 1429 (m), 1420 (m), 1394 (m), 1373 (m), 1367 (m), 1324 (m), 1273 (s), 1129 (m), 1066 (m), 1058 (m), 1040 (s, Cp), 939 (m), 923 (m), 786 (vs), 753 (m), 730 (s), 709 (m). Anal Calcd for $C_{17}H_{21}Ti$: C, 74.73; H, 7.75. Found C, 74.46; H, 8.04.

ansa-[1]-Titanocene Crotyl 100 from Titanocene Chloride 92:

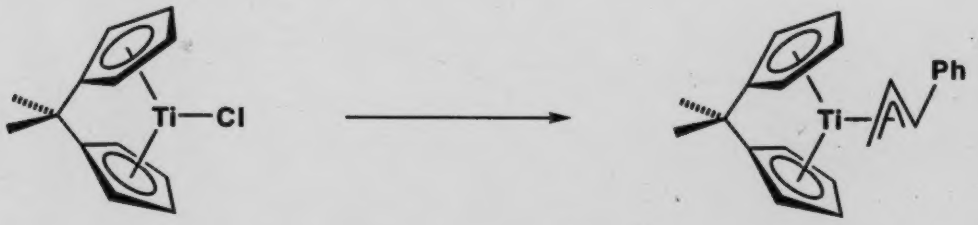


92 **100**

***ansa*-[1]-{Dimethylmethano bis(cyclopentadienyl)}titanium crotyl 100.** In the drybox, a 50 mL round bottom flask containing (15 mL) *ansa*-[1]-{dimethylmethano bis(cyclo-pentadienyl)}titanium chloride **92** (1.035 g, 2.04 mmol) in 20 mL of THF was cooled to -35 °C. Crotylmagnesium chloride (1.36 mL, 1.5 M in THF) was added *via* syringe to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The solvent was removed *in vacuo* and the resulting dark purple residue was triturated with pentane (5 x 5 mL) and the solution filtered through a sintered-glass funnel layered with celite. Concentration of the filtrate and cooling to -35 °C yielded dark purple needles (400 mg, 72%). This air-sensitive paramagnetic complex was characterized by infrared spectroscopy and elemental analysis: IR (cm^{-1}, KBr, cast):

2670 (m), 1531 (w, η^3-allyl),[115,213] 1468 (m), 1451 (m), 1433 (m), 1422 (w), 1381 (s), 1367 (m), 1273 (s), 1231 (w), 1205 (m), 1147 (w), 1129 (s), 1109 (m), 1063 (m), 1054 (m), 1044 (m), 1027 (m), 1007 (m), 975 (w), 938 (m), 902 (w), 874 (m), 837 (s), 820 (m), 790 (vs), 740 (m), 729 (vs), 709 s, 666 (w). Anal Calcd for $C_{17}H_{21}Ti$: C, 74.73; H, 7.747. Found C, 74.95; H, 7.94.

***ansa*-[1]-Titanocene Cinnamyl 101 from Titanocene Chloride 92:**

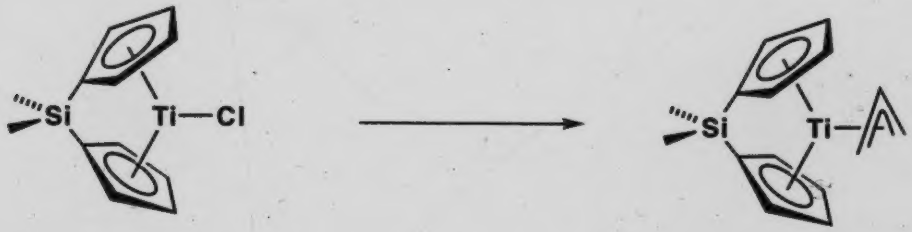


92

101

***ansa*-[1]-{Dimethylmethano bis(cyclopentadienyl)}titanium cinnamyl 101**. In the drybox, a 25 mL round bottom flask containing a solution (10 mL) of *ansa*-[1]-{dimethylmethano bis(cyclopentadienyl)}titanium chloride **92** (286 mg, 0.564 mmol) was cooled to -35 °C. To this solution was added a cooled solution (-35 °C) of cinnamyllithium (140 mg, 1.13 mmol). The resulting reaction mixture was allowed to warm to room temperature and stirred for 3 h. The solvent was removed *in vacuo* and the dark blue residue obtained was extracted with pentane (5 x 5 mL). Filtration, concentration, and cooling (-35 °C) of the pentane filtrate gave dark blue needles (32.0 mg, 21%). This extremely air-sensitive paramagnetic complex was characterized by infrared spectroscopy and high resolution mass spectrometry: IR (cm^{-1}, KBr, cast): 3093 (w), 3080 (w), 3057 (w), 3022 (w), 2959 (m), 2921 (m), 2869 (m), 1594 (m), 1529 (m), 1493 (m), 1470 (w), 1450 (m), 1419 (w), 1381 (w), 1367 (m), 1272 (m), 1248 (m), 1039 (m), 794 (vs), 754 (s), 731 (s), 710 (m), 695 (vs). MS Calcd for $C_{22}H_{23}Ti$ *m/e* 335.12792. No molecular ion was observed, however, important fragment ions that strongly suggests the elemental composition of complex **101** include 218.05803 ((0.1%), $C_{13}H_{14}Ti$, titanocene template); 117.07059 ((100%), C_9H_9, cinnamyl ligand).

ansa-[1]-Titanocene Allyl 102 from Titanocene Chloride 93:

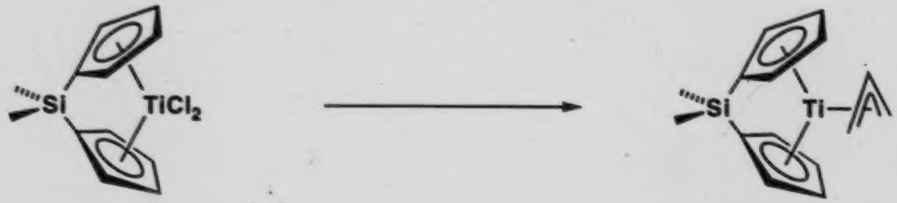


93

102

***ansa*-[1]{Dimethylsilyl bis(cyclopentadienyl)}titanium allyl 102.** In the drybox, a 50 mL round bottom flask containing *ansa*-[1]-{dimethylsilyl bis(cyclopentadienyl)}-titanium chloride **93** (498 mg, 0.924 mmol) in THF (20 mL) was cooled to -35 °C. Allylmagnesium chloride (924 µL, 2 M in THF) was added to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The solvent was removed *in vacuo* and the dark purple residue obtained was triturated with pentane (5 x 5 mL). Filtration, concentration, and cooling (-35 °C) of the pentane filtrate gave violet needles (43.3 mg, 8.5%). This extremely air-sensitive paramagnetic complex was partially characterized by infrared spectroscopy: IR (cm^{-1}, KBr, cast): 2955 (m), 1509 (m, η^3-allyl),[115,213] 1452 (w), 1364 (m), 1251 (s), 1174 (s), 1097 (m), 1060 (m), 1044 (s), 1028 (s, Cp), 899 (m), 829 (s), 797 (vs), 751 (s), 673 (s), 636 (m).

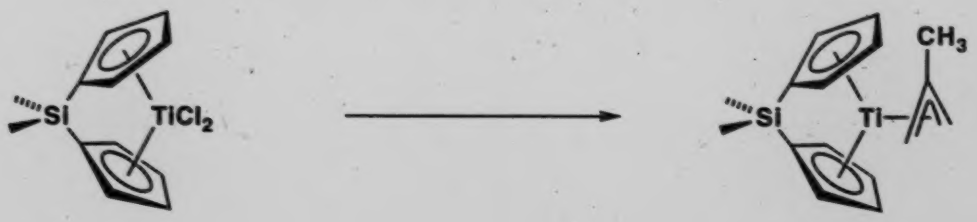
ansa-[1]-Titanocene Allyl 102 from *ansa*-[1]-Titanocene Dichloride:



102

***ansa*-[1]{Dimethylsilyl bis(cyclopentadienyl)}titanium allyl 102.** In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of *ansa*-[1]-{dimethylsilyl bis(cyclopentadienyl)}titanium dichloride[111,112] (42.0 mg, 0.156 mmol) was cooled to -35 °C. Allylmagnesium chloride (153 µL, 2 M in THF) was added to this cooled solution and the resulting purple reaction mixture was allowed to warm to room temperature, stirred for 20 minutes and then heated at reflux for a further 20 minutes. The solvent was removed *in vacuo* from the resulting violet solution, yielding a violet residue, which was triturated with pentane (4 x 5 mL) and the solution filtered through a short column of celite. Concentration of the pentane filtrate and cooling to -35 °C gave complex **102** as violet needles (28.0 mg, 71%). Characterization is given above.

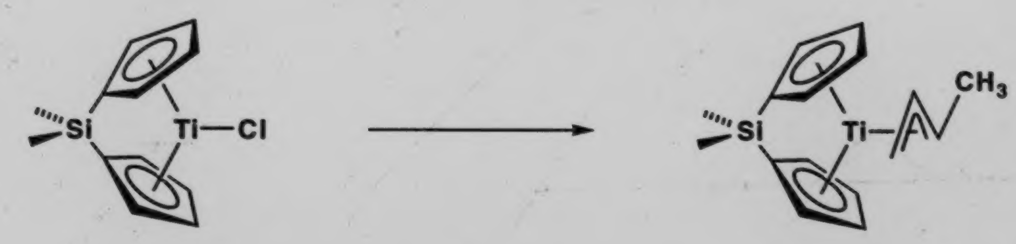
ansa-[1]-Titanocene 2-Methylallyl 103 from *ansa*-[1]-Titanocene Dichloride:



103

***ansa*-[1]{Dimethylsilyl bis(cyclopentadienyl)}titanium 2-methylallyl 103**. In the drybox, a 25 mL round bottom flask containing a THF solution (5 mL) of *ansa*-[1]-{dimethylsilyl bis(cyclopentadienyl)}titanium dichloride[111,112] (28.0 mg, 0.0918 mmol) was cooled to -35 °C. 2-Methylallylmagnesium chloride (153 μL, 1.5 M in THF) was added to the cooled solution by syringe and the resulting reaction mixture was allowed to warm to room temperature and subsequently heated at reflux for 20 minutes. The solvent was removed *in vacuo* and the dark purple residue obtained was triturated with pentane (5 x 5 mL). Filtration of the pentane solution through a short column of celite, concentration and cooling to -35 °C yielded dark purple needles (6.8 mg, 26%). This air-sensitive paramagnetic complex was partially characterized by infrared spectroscopy: IR (cm^{-1}, KBr, cast): 2953 (m), 1489 (m, η^3-allyl),[115,213] 1432 (m), 1409 (m), 1365 (m), 1250 (s), 1178 (s), 1064 (m), 1048 (s), 1037 (s, Cp), 901 (m), 874 (w), 827 (s), 801 (vs), 791 (vs), 763 (s), 626 (m), 579 (s).

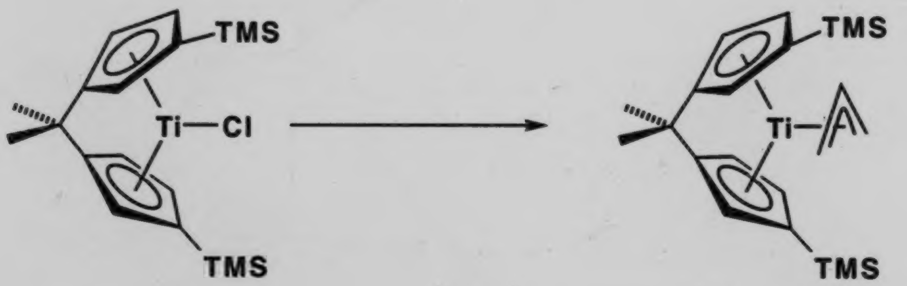
***ansa*-[1]-Titanocene Crotyl 104 from Titanocene Chloride 93**:



93 104

***ansa*-[1]{Dimethylsilyl bis(cyclopentadienyl)}titanium crotyl 104**. In the drybox, a 50 mL round bottom flask containing a THF solution (20 mL) of *ansa*-[1]-{dimethylsilyl bis(cyclopentadienyl)}titanium chloride **93** (512 mg, 0.950 mmol) was cooled to -35 °C. Crotylmagnesium chloride (1.3 mL, 1.5 M in THF) was added to this cooled solution and the resulting reaction mixture was allowed to warm to room temperature and then stirred for 1.5 h. The solvent was removed *in vacuo* yielding a dark purple residue, which was triturated with pentane (4 x 5 mL). Filtration of the pentane solution through a short column of celite, concentration of the pentane filtrate and cooling to -35 °C afforded dark purple needles (69.0 mg, 13%). This air-sensitive paramagnetic complex was used without further characterization.

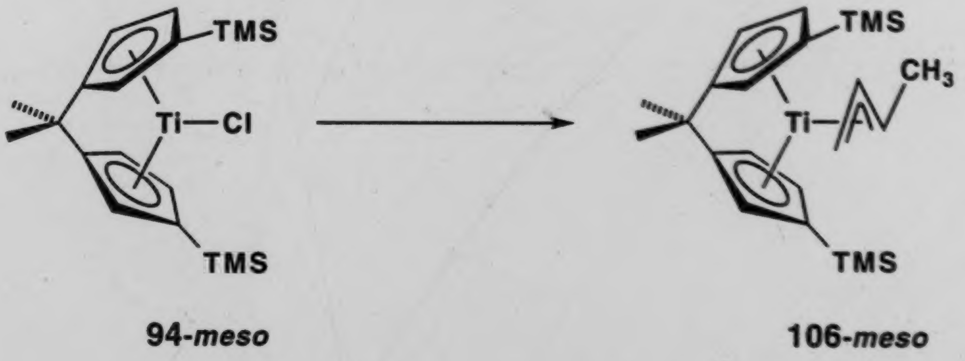
***Meso ansa*-[1]-Titanocene Allyl 105-*meso* from Titanocene Chloride 94-*meso* :**



94-*meso*   105-*meso*

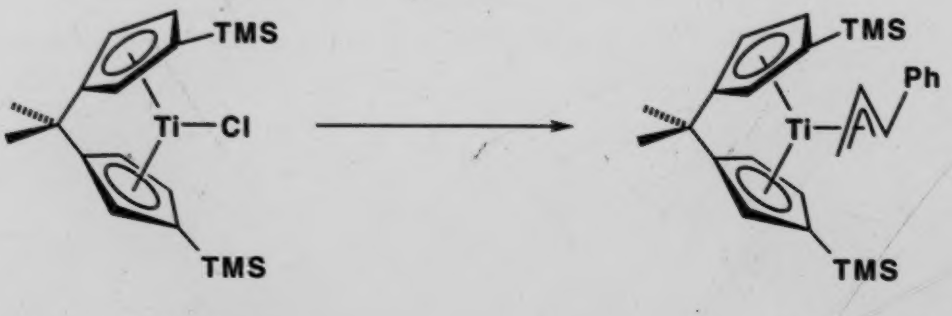
Meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium allyl 105-*meso*.** In the drybox, a 25 mL round bottom flask containing a THF solution (5 mL) of *meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium chloride **94-*meso (60 mg, 0.0758 mmol) was cooled to -35 °C. Allylmagnesium chloride (87 µL, 2 M in THF) was added to this solution and after 10 minutes at -35 °C, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Removal of the solvent *in vacuo* yielded a dark purple residue which was triturated with pentane and the solution filtered through a sintered-glass funnel layered with celite. Concentration of the filtrate and cooling to -35 °C yielded dark purple cubes (50.0 mg, 82%). This air-sensitive paramagnetic allyl complex was characterized by infrared spectroscopy and elemental analysis: IR (cm^{-1}, KBr, cast): 3077 (w), 3067 (w), 2951 (m), 2876 (w), 1504 (w, η^3-allyl),[115,213] 1470 (w), 1445 (w), 1405 (w), 1384 (w), 1368 (w), 1245 (s), 1173 (w), 1152 (w), 1089 (w), 1079 (w), 1055 (w), 1004 (w), 922 (m), 838 (vs), 813 (s), 790 (m), 773 (m), 755 (m), 736 (w), 726 (m), 714 (w), 693 (w), 668 (m), 628 (m), 463 (w). Anal Calcd for $C_{22}H_{35}Si_2Ti$: C, 65.48; H, 8.74. Found C, 65.38; H, 8.94.

***Meso ansa*-[1]-Titanocene Crotyl 106-*meso* from Titanocene Chloride 94-*meso* :**



Meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium crotyl 106-*meso . In the drybox, a 50 mL round bottom flask containing a THF solution (20 mL) of *meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}-titanium chloride **94-*meso*** (330 mg, 0.829 mmol) was cooled to -35 °C. Crotylmagnesium chloride (600 µL, 1.24 mmol, 1.5 M in THF) was added to this cooled solution and after 10 minutes at -35 °C, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Removal of the solvent *in vacuo* yielded a dark purple residue which was triturated with pentane and the solution filtered through a sintered-glass funnel layered with celite. Concentration of the filtrate and cooling to -35 °C yielded dark purple cubes (248 mg, 72%). This air-sensitive paramagnetic crotyl complex was characterized by infrared spectroscopy and elemental analysis: IR (cm^{-1}, KBr, cast): 2955 (s), 2927 (m), 2908 (m), 2874 (m), 2851 (m), 1560 (w), 1549 (w, η^3-allyl),[115,213] 1475 (w), 1401 (m), 1368 (m), 1280 (w), 1248 (s), 1173 (m), 1154 (m), 1090 (m), 1079 (w), 1054 (w), 924 (m), 837 (vs), 816 (s), 793 (m), 777 (m), 753 (s), 734 (m), 727 (m), 689 (m), 508 (m). Anal Calcd for $C_{23}H_{37}Si_2Ti$: C, 66.15; H, 8.93. Found C, 65.98; H, 8.90.

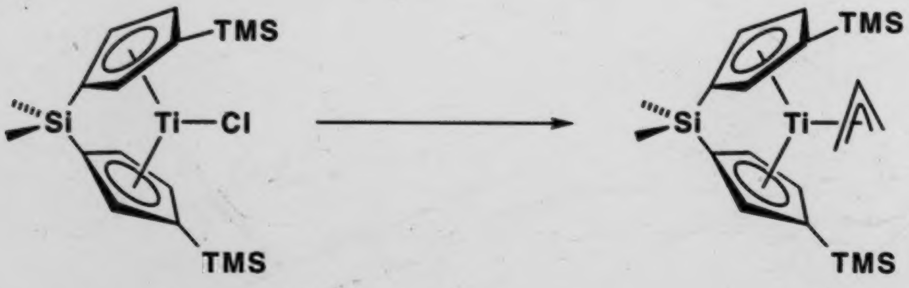
***Meso ansa*-[1]-Titanocene Cinnamyl 107-*meso* from Titanocene Chloride 94-*meso* :**



94-*meso*　　**107-*meso***

Meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium cinnamyl 107-*meso . In the drybox, a 50 mL round bottom flask containing a THF solution (30 mL) of *meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilyl-cyclopentadienyl)}titanium chloride **94-*meso*** (200 mg, 0.503 mmol) was cooled to -35 °C. A cooled THF solution (5 mL) of cinnamyllithium (62.4 mg, 0.503 mmol) was then added to the solution of the monochloride and after 30 minutes at -35 °C, the reaction mixture was allowed to warm to room temperature and subsequently stirred for 1 h. Removal of the solvent *in vacuo* yielded a dark blue residue, which was triturated with pentane and the solution filtered through a sintered-glass funnel layered with celite. Concentration of the filtrate and cooling to -35 °C yielded dark blue needles (80.0 mg, 33%). This air-sensitive paramagnetic cinnamyl complex was characterized by infrared spectroscopy and elemental analysis: IR (cm^{-1}, KBr, cast): 2953 (s), 2896 (m), 2871 (m), 1597 (m), 1534 (m), 1369 (m), 1247 (s), 1173 (m), 1153 (m), 1090 (m), 923 (m), 838 (vs), 796 (m), 754 (s), 736 (m), 728 (m). Anal Calcd for $C_{28}H_{39}Si_2Ti$: C, 70.11; H, 8.2. Found C, 69.73; H, 8.6.

Meso ansa-[1]-Titanocene Allyl 108-*meso* from Titanocene Chloride 97-*meso*:

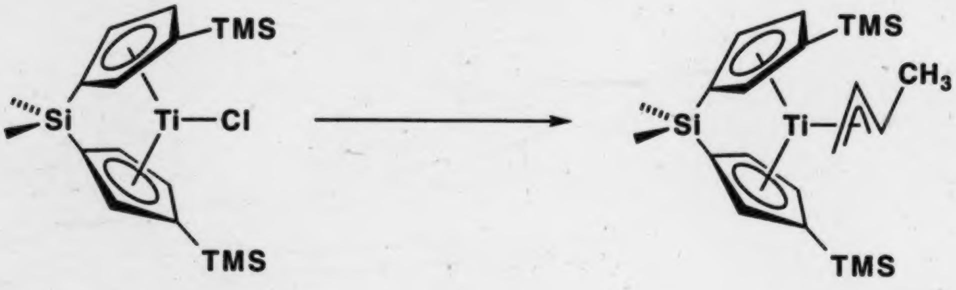


92-*meso* **108-*meso***

Meso ansa*-[1]-{dimethylsilylbis(3-trimethylsilylcyclopentadienyl)}titanium allyl 108-*meso*.** In the drybox, a 50 mL round bottom flask containing a THF solution (30 mL) of *meso ansa*-[1]-{dimethylsilylbis(3-trimethylsilylcyclopentadienyl)}titanium chloride **97-*meso (131 mg, 0.315 mmol) was cooled to -35 °C. Allylmagnesium chloride (600 μL, 2 M in THF) was added to this cooled solution and after 10 minutes at -35 °C, the reaction mixture was allowed to warm to room temperature and subsequently stirred for 1 h. Removal of the solvent *in vacuo* yielded a dark purple residue which was triturated with pentane and the solution filtered through a sintered-glass funnel layered with celite. Concentration of the filtrate and cooling to -35 °C yielded dark purple cubes (125 mg, 94%). This air-sensitive paramagnetic allyl complex was partially characterized by infrared spectroscopy: IR (cm^{-1}, KBr, cast): 2954 (m), 2897 (w), 1509 (w, η^3-

allyl),[115,213] 1445 (w), 1265 (m), 1247 (s), 1208 (w), 1086 (s), 1054 (w), 924 (m), 831 (vs), 803 (s), 784 (m), 755 (m), 670 (m).

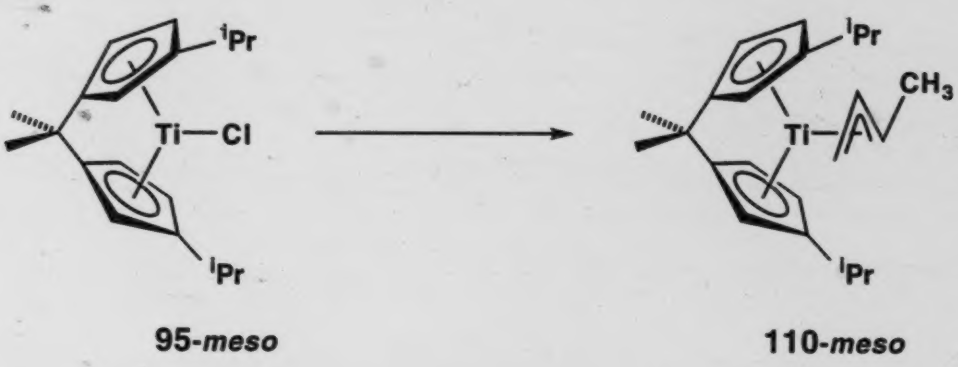
***Meso ansa*-[1]-Titanocene Crotyl 109-*meso* from Titanocene Chloride 97-*meso*:**



97-*meso* **109-*meso***

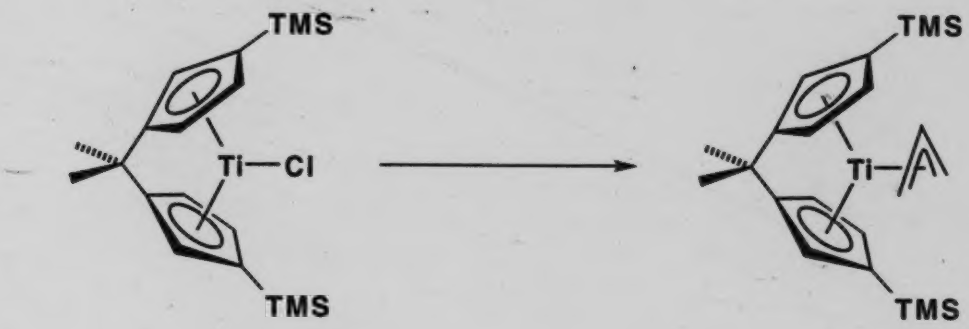
Meso ansa*-[1]-{dimethylsilylbis(3-trimethylsilylcyclopentadienyl)}titanium crotyl 109-*meso*.** In the drybox, a 50 mL round bottom flask containing a THF solution (30 mL) of *meso ansa*-[1]-{dimethylsilylbis(3-trimethylsilylcyclopentadienyl)}titanium chloride **97-*meso (140 mg, 0.34 mmol) was cooled to -35 °C. Crotylmagnesium chloride (226 µL, 1.5 M in THF) was added to the cooled solution and after 10 minutes at -35 °C, the reaction mixture was allowed to warm to room temperature and subsequently stirred for 1 h. Removal of the solvent yielded a dark purple residue which was triturated with pentane and the solution filtered through a sintered-glass funnel layered with celite. Concentration of the filtrate and cooling to -35 °C yielded dark purple cubes (147 mg, quant.). This air-sensitive paramagnetic crotyl complex was characterized by infrared spectroscopy and high resolution mass spectrometry: IR (cm^{-1}, KBr, cast): 3035 (m), 2953 (s), 2924 (m), 2897 (m), 2851 (m), 1534 (w, η^3-allyl),[115,213] 1444 (m), 1405 (m), 1384 (w), 1374 (w), 1324 (w), 1266 (s), 1246 (vs), 1208 (m), 1087 (vs), 1053 (m), 1024 (m), 927 (s), 881 (m), 832 (vs), 803 (s), 785 (s), 754 (s), 733 (m), 691 (m), 670 (s), 638 (m), 482 (m), 474 (m). MS Calcd for $C_{22}H_{37}Si_3Ti$ *m/e* 433.16824, found 433.16907.

***Meso ansa*-[1]-Titanocene Crotyl 110-*meso* from Titanocene Chloride 95-*meso* :**



Meso ansa*-[1]-{dimethylmethano bis(3-isopropylcyclopentadienyl)}titanium crotyl 110-*meso . In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of *meso ansa*-[1]-{dimethylmethano bis(3-isopropylcyclopentadienyl)}titanium chloride **95-*meso*** (77.6 mg, 0.23 mmol) was cooled to -35 °C. Crotylmagnesium chloride (154 µL, 1.5 M in THF) was added to this cooled solution and after 10 minutes at this temperature, the reaction mixture was allowed to warm to room temperature and subsequently stirred for 2 h. Removal of the solvent *in vacuo* yielded a dark purple residue which was triturated with pentane and the solution filtered through a short column of celite. The pentane filtrate was concentrated and cooled to -35 °C, yielding dark purple needles (76.0 mg, 92%). This air-sensitive paramagnetic crotyl complex was characterized by infrared spectroscopy and elemental analysis: IR (cm^{-1}, KBr, cast): 2958 (vs), 2923 (vs), 2868 (vs), 2849 (vs), 1529 (w, η^3-allyl),[115,213] 1496 (w), 1455 (m), 1424 (w), 1371 (m), 1358 (m), 1298 (w), 1284 (m), 1204 (m), 1107 (w), 1051 (m), 1042 (m), 831 (m), 811 (vs), 798 (s), 766 (m), 726 (s). Anal Calcd for $C_{23}H_{33}Ti$: C, 77.3; H, 9.31. Found C, 77.22; H, 9.51.

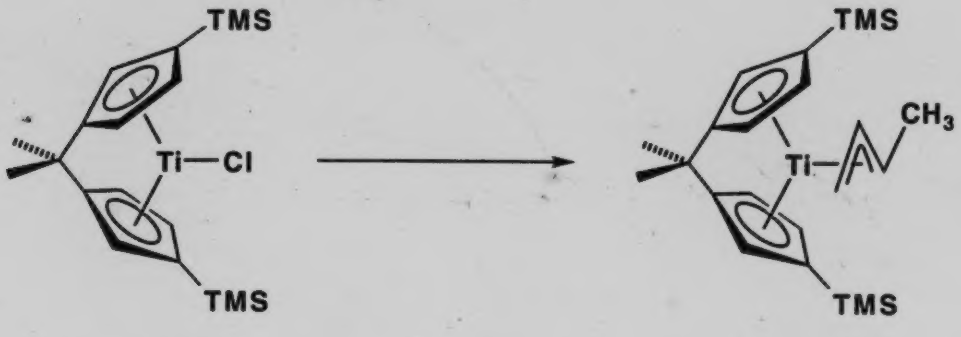
***Rac ansa*-[1]-Titanocene Allyl 105-*rac* from Titanocene Chloride 94-*rac*:**



94-*rac* **105-*rac***

Rac ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium allyl 105-*rac. In the drybox, a 50 mL round bottom flask containing a THF solution (20 mL) of *rac ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium chloride **94-*rac*** (101 mg, 0.127 mmol) was cooled to -35 °C. Allylmagnesium chloride (145 μL, 2.0 M in THF) was added to the cooled solution and after 10 minutes at this temperature, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Removal of the solvent *in vacuo* yielded a dark purple residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded purple needles (68.0 mg, 66%). This air-sensitive paramagnetic allyl complex was characterized by infrared spectroscopy and elemental analysis: IR (cm^{-1}, KBr, cast): 2952 (m), 2895 (w), 2876 (w), 1505 (m, η^3-allyl),[115,213] 1369 (w), 1252 (m), 1244 (m), 1174 (m), 1153 (m), 1089 (m), 1079 (w), 923 (m), 837 (m), 814 (m), 790 (m), 773 (m), 754 (m), 734 (m), 727 (m), 693 (w), 633 (w). Anal Calcd for $C_{22}H_{35}Si_2Ti$: C, 65.48; H 8.74. Found C, 65.28; H, 8.92.

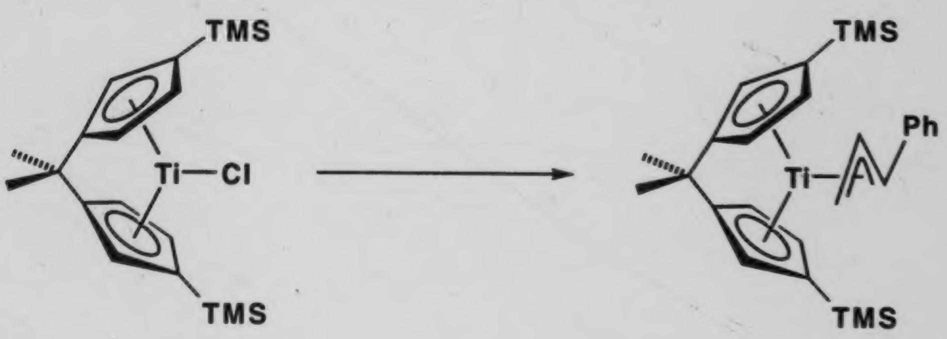
***Rac ansa*-[1]-Titanocene Crotyl 106-*rac* from Titanocene Chloride 94-*rac*:**



94-*rac* **106-*rac***

Rac ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium crotyl 106-*rac*.** In the drybox, a 50 mL round bottom flask containing a THF solution (20 mL) of *rac ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}-titanium chloride **94-*rac (117.4 mg, 0.295 mmol) was cooled to -35 °C. Crotylmagnesium chloride (197 µL, 1.5 M in THF) was added to the cooled solution and after 10 minutes at this temperature, the reaction mixture was allowed to warm to room temperature and subsequently stirred for 1 h. Removal of the solvent *in vacuo* yielded a dark purple residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded purple needles (70.0 mg, 57%). This air-sensitive paramagnetic crotyl complex was characterized by infrared spectroscopy and elemental analysis: IR (cm^{-1}, KBr, cast): 2953 (m), 2921 (m), 2873 (m), 2851 (m), 1551 (w, η^3-allyl),[115,213] 1472 (w), 1452 (w), 1444 (w), 1410 (w), 1368 (m), 1247 (s), 1199 (w), 1155 (m), 1086 (m), 1077 (m), 1057 (m), 1024 (m), 922 (m), 836 (vs), 812 (s), 787 (m), 754 (m), 727 (m). Anal Calcd for $C_{28}H_{39}Si_2Ti$: C, 66.15; H, 8.93. Found C, 66.02; H, 9.23.

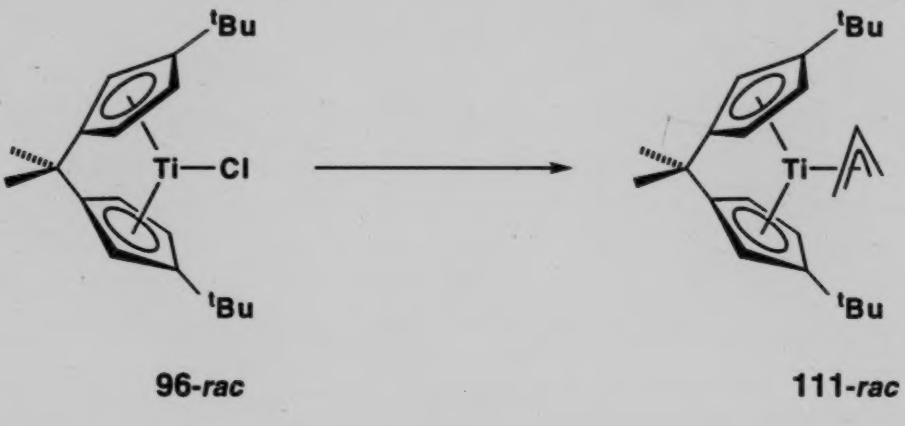
Rac ansa-[1]-Titanocene Cinnamyl 107-*rac* from Titanocene Chloride 94-*rac*:



94-*rac* **107-*rac***

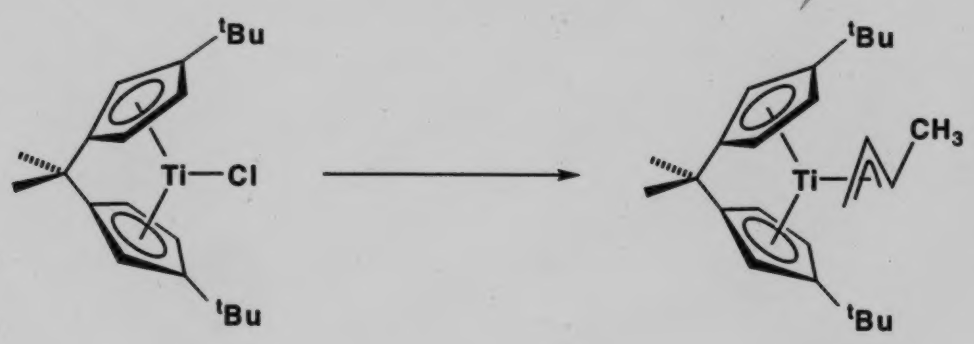
Rac ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium cinnamyl 107-*rac*.** In the drybox, a 50 mL round bottom flask containing a THF solution (30 mL) of *rac ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}-titanium chloride **94-*rac (1.1062 g, 2.78 mmol) was cooled to -35 °C. A cooled THF solution of cinnamyllithium (345 mg, 2.78 mmol) was added to the monochloride solution and after 30 minutes at this temperature, the reaction mixture was allowed to warm to room temperature and subsequently stirred for 1 h. Removal of the solvent *in vacuo* yielded a dark blue residue which was triturated with pentane and the solution filtered through a sintered-glass funnel layered with celite. Concentration of the filtrate and cooling to -35 °C afforded dark blue needles (1.10 g, 83%). This air-sensitive paramagnetic cinnamyl complex was characterized by infrared spectroscopy and high resolution mass spectrometry: IR (cm^{-1}, KBr, cast): 3076 (w), 3025 (w), 2954 (m), 2896 (m), 2871 (m), 1597 (m), 1533 (m), 1471 (w), 1448 (m), 1405 (m), 1369 (m), 1248 (s), 1171 (m), 1154 (m), 1087 (m), 1076 (m), 923 (m), 837 (vs), 798 (m), 790 (m), 755 (m), 732 (m), 695 (m), 633 (m). MS Calcd for $C_{28}H_{39}Si_2Ti$ *m/e* 479.20697, found 479.20666.

***Rac ansa*-[1]-Titanocene Allyl 111-*rac* from Titanocene Chloride 96-*rac*:**



Rac ansa*-[1]-{dimethylmethano bis(3-*tert*-butylcyclopentadienyl)}titanium allyl 111-*rac*.** In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of *rac ansa*-[1]-{dimethylmethano bis(3-*tert*-butylcyclopentadienyl)}titanium chloride **96-*rac (50.8 mg, 0.139 mmol) was cooled to -35 °C. Allylmagnesium chloride (90 μL, 2 M in THF) was added to the cooled solution and after 10 minutes at this temperature, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Removal of the solvent *in vacuo* yielded a dark purple residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded purple needles (31.0 mg, 60%). This air-sensitive paramagnetic allyl complex was characterized by infrared spectroscopy and elemental analysis: IR (cm^{-1}, KBr, cast): 2960 (vs), 2903 (w), 2868 (w), 1496 (m, η^3-allyl),[115,213] 1461 (m), 1375 (m), 1358 (m),1280 (w), 1248 (s), 1195 (m), 806 (vs), 728 (s). Anal Calcd for $C_{24}H_{35}Ti$: C, 77.62; H, 9.5. Found C, 77.84; H, 9.49.

***Rac ansa*-[1]-Titanocene Crotyl 112-*rac* from Titanocene Chloride 96-*rac*:**

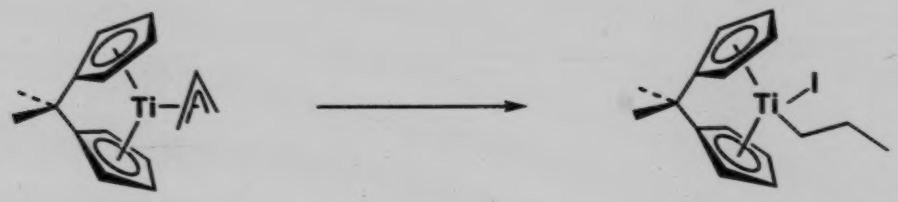


96-*rac* **112-*rac***

Rac ansa*-[1]-{dimethylmethano bis(3-*tert*-butylcyclopentadienyl)}titanium crotyl 112-*rac*.** In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of *rac ansa*-[1]-{dimethylmethano bis(3-*tert*-butylcyclopentadienyl)}titanium chloride **96-*rac (27.0 mg, 0.0741 mmol) was cooled to -35 °C. Crotylmagnesium chloride (49 μL, 1.5 M in THF) was added to the cooled solution and after 10 minutes at this temperature, the reaction mixture was allowed to warm to room temperature and subsequently stirred for 1 h. Removal of the solvent *in vacuo* yielded a dark purple residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded purple needles (17.4 mg, 61%). This air-sensitive paramagnetic crotyl complex was characterized by infrared spectroscopy and high resolution mass spectrometry: IR (cm^{-1}, KBr, cast): 3073 (m), 2960 (vs), 2926 (vs), 2904 (vs), 2871 (vs), 1627 (m), 1605 (m), 1552 (m), 1535 (m, η^3-allyl),[115,213] 1493 (m), 1460 9s), 1425 (m), 1387 (s), 1375 (s), 1359 (s), 1295 (m), 1283 (m), 1249 (s), 1222 (m), 1195 (s), 1160 (m), 1154 (m), 1026 (s), 996 (m), 956 (m), 940 (s), 918 (m), 882 (s), 852 (m), 837 (s), 806 (vs), 773 (m), 759 (m), 726 (vs), 714 (m), 676 (m), 635 (m). MS Calcd for $C_{25}H_{37}Ti$ *m/e* 385.23749, found 385.23745. Other important ions include 330.18317 ((100%), $C_{21}H_{30}Ti$, titanocene template); 57.07063 ((4%), C_4H_9); 55.05442((6%), C_4H_7, crotyl ligand).

2.3.3. Radical Addition to *ansa*-bridged Titanium(III) η^3-Allyl Complexes

ansa-[1]-Titanocene (*n*-propyl) iodide 113 from Allyl Complex 98:

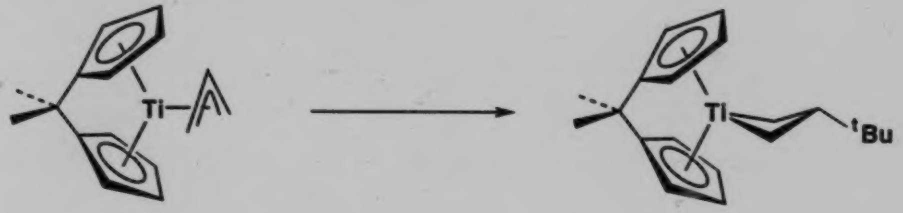


98

113

***ansa*-[1]-{Dimethylmethano bis(cyclopentadienyl)}titanium (*n*-propyl) iodide 113**. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of *ansa*-[1]-{dimethylmethano bis(cyclopentadienyl)}titanium allyl **98** (21.0 mg, 0.0810 mmol) and SmI_2 (0.8 mL, 0.1 M in THF) was cooled to -35 °C. *n*-Propyl iodide (8.0 µL) was added to the cooled solution *via* a micro-syringe. The reaction mixture was allowed to warm to room temperature and stirred for 1.5 h during which time the color gradually changed from dark blue to burgundy. The solvent was removed *in vacuo* and the burgundy residue was triturated with pentane (4 x 5 mL). The combined extracts were filtered through a short column of celite, concentrated and cooled to -35 °C to yield burgundy micro-needles (16.0 mg, 51%). Spectroscopic and analytical data for complex **113**: ^1H NMR (400.1 MHz, C_6D_6): δ 7.64 (dd, J = 3.2, 5.4 Hz, 2H, $C_5\underline{H}_3$), 6.73 (dd, J = 3.2, 5.2 Hz, 2H, $C_5\underline{H}_3$), 4.79 (dd, J = 2.7, 4.8 Hz, 2H, $C_5\underline{H}_3$), 4.58 (dd, J = 2.6, 5.0 Hz, 2H, $C_5\underline{H}_3$), 1.35 (m, 2H, $C\underline{H}_2CH_2CH_3$), 1.11 (m, 2H, $CH_2C\underline{H}_2CH_3$), 0.92 (s, 3H, $C(CH_3)_2$), 0.82 (t, J = 6.2 Hz, 3H, $CH_2CH_2C\underline{H}_3$), 0.80 (s, 3H, $C(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, APT): δ 125.3 ($\underline{C}_5H_3$), 123.4 ($\underline{C}_5H_3$), 112.2 (C_q, $\underline{C}_5H_3$), 109.6 ($\underline{C}_5H_3$), 109.2 ($\underline{C}_5H_3$), 87.6 ($\underline{C}H_2CH_2CH_3$), 35.5 ($\underline{C}(CH_3)_2$), 29.9 ($CH_2\underline{C}H_2CH_3$), 23.0 ($CH_2CH_2\underline{C}H_3$), 22.3 ($C(\underline{C}H_3)_2$), 19.7 ($C(\underline{C}H_3)_2$). IR (cm^{-1}, KBr, cast): 3418 (m), 3384 (m), 2954 (m), 1456 (m), 1417 (m), 1395 (m), 1383 (m), 1271 (m), 1167 (m), 1151 (m), 1106 (s), 1046 (s), 838 (m), 821 (vs), 798 (vs), 762 (m), 737 (m), 710 (m). Anal Calcd for C, 49.51; H, 5.45 ($C_{16}H_{21}TiI$). Found C, 50.28; H, 5.42.

Titanacyclobutane 117 from Allyl Complex 98:

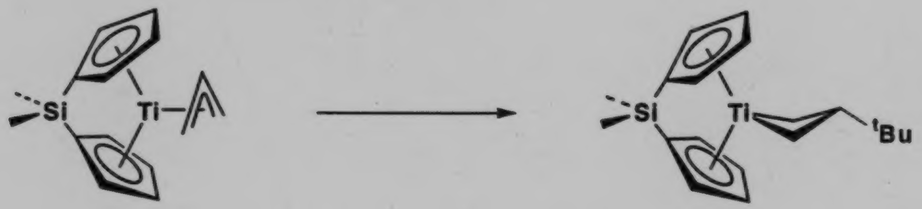


98 **117**

3-*tert*-Butyl *ansa*-[1]-{dimethylmethano bis(cyclopentadienyl)}titanacyclobutane 117. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of *ansa*-[1]-{dimethylmethano bis(cyclopentadienyl)}titanium allyl **98** (68.2 mg, 0.263 mmol) and SmI_2 (2.7 mL, 0.1 M in THF) was cooled to -35 °C. 2-Chloro-2-methylpropane (1 equivalent) was added to the cooled solution and after 10 minutes at -35 °C, the reaction mixture was allowed to warm to room temperature and stirred for 2 h. The mixture gradually changed color from blue to red-brown. The solvent was removed *in vacuo* and the reddish-brown residue was triturated with pentane. The pentane solution was filtered through a short column of celite and the filtrate concentrated and cooled to -35 °C to yield a red-brown micro-crystalline solid (44.0 mg, 51%). Spectroscopic and analytical data for titanacyclobutane **117**: ^1H NMR (400.1 MHz, C_6D_6): δ 5.99 (t, J = 2.5 Hz, 1H, Cp), 5.82 (t, J = 2.5 Hz, 1H, Cp), 5.23 (t, J = 2.5 Hz, 1H, Cp), 5.13 (t, J = 2.5 Hz, 1H, $C_5\underline{H}_3$), 2.73 (t, J = 10.0 Hz, 2H, α-CH_2), 2.32 (t, J = 10.0 Hz, 2H, α-CH_2), 1.22 (s, 6H, $C(C\underline{H}_3)_2$), 1.03 (s, 9H, $C(C\underline{H}_3)_3$), 0.06 (quintet, J =

10.0 Hz, 1H, β-CH). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, APT): δ 117.1 ($Cp_{methine}$), 117.0 ($Cp_{methine}$), 112.2 ($Cp_{quaternary}$), 111.2 ($Cp_{quaternary}$), 104.8 ($Cp_{methine}$), 103.6 ($Cp_{methine}$), 73.7 (α-CH_2), 36.2 ($\underline{C}(CH_3)_2$), 34.1 ($\underline{C}(CH_3)_3$), 29.3 (β-CH), 23.5 ($C(\underline{C}H_3)_3$), 18.9 ($C(\underline{C}H_3)_2$). IR (cm^{-1}, KBr, cast): 2962 (m), 2932 (m), 2860 (m), 1356 (m), 1271 (m), 1211 (m), 1095 (m), 1060 (m), 1045 (s), 879 (m), 860 (m), 801 (vs), 738 (s), 717 (m). Anal Calcd for C, 75.94; H, 8.92. Found C, 75.91; H, 8.94.

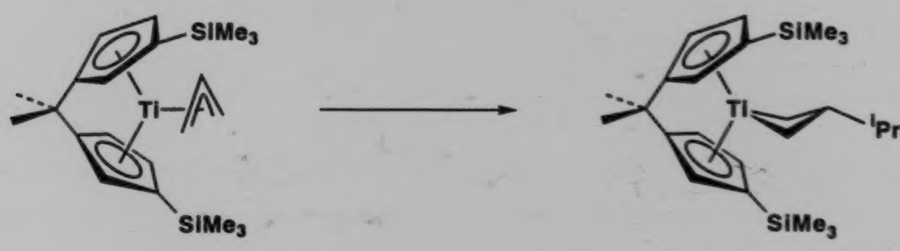
Titanacyclobutane 118 from Allyl Complex 99:



99 **118**

***tert*-Butyl *ansa*-[1]-{dimethylsilylbis(cyclopentadienyl)}titanacyclobutane 118**. In the drybox, a THF solution (20 mL) of *ansa*-[1]-{dimethylsilyl bis(cyclopentadienyl)}-titanium allyl **99** (22.0 mg, 0.0788 mmol) and SmI_2 (0.79 mL, 0.1 M in THF) in a 50 mL round bottom flask was treated with 2-chloro-2-methylpropane (1 equivalent) at room temperature. The reaction mixture was stirred at this temperature for 2 h during which time the mixture gradually changed color from blue to red-brown. The solvent was removed *in vacuo* and the reddish-brown residue was triturated with pentane. The pentane solution was filtered through a short column of celite. The filtrate was concentrated and cooled to -35 °C, yielding a red-brown microcystalline solid (10.0 mg, 38%). Spectroscopic and high resolution mass spectrometry data for titanacyclobutane **118**: ^1H NMR (C_6D_6, 400.1 MHz): δ 6.34 (t, J = 2.2 Hz, 2H, Cp), 6.15 (t, J = 2.2 Hz, 2H, Cp), 5.55 (t, J = 2.2 Hz, 2H, Cp), 5.44 (t, J = 2.2 Hz, 2H, Cp), 2.49 (t, J = 10.0 Hz, 2H, α-CH_2), 2.18 (t, J = 10.0 Hz, 2H, α-$\mathrm{C}H_2$), 0.98 (s, 3H, $\mathrm{Si(C}H_3)_2$), 0.18 (s, 3H, $\mathrm{Si(C}H_3)_2$), -0.02 (quintet, J = 10.0 Hz, 1H, β-$\mathrm{C}H$). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, APT): δ 121.4 ($Cp_{methine}$), 121.3 ($Cp_{methine}$), 111.7 ($Cp_{methine}$), 111.6 ($Cp_{methine}$), 100.6 ($Cp_{quaternary}$), 99.6 ($Cp_{quaternary}$), 70.4 (α-CH_2), 33.9 ($\underline{C}(CH_3)_3$), 29.2 (β-CH), 17.3 ($C(\underline{C}H_3)_3$), -5.4 ($Si(\underline{C}H_3)_2$). IR (cm^{-1}, KBr, cast): 2958 (m), 2900 (m), 2861 (m), 1357 (w), 1294 (w), 1254 (m), 1174 (m), 1051 (m), 812 (vs), 669 (m). MS Calcd for $C_{19}H_{28}SiTi$ *m/e* 332.14398, found 332.14274. Other important ions include 275.07271 (M^+-57 (90%), $C_{15}H_{19}SiTi$, the titanacyclobutane moiety less the β-*tert*-butyl substituent), 234.03360 ((10%), $C_{12}H_{14}SiTi$, the titanocene template); 84.09141 ((10%), C_6H_{12}, 3,3-dimethylbutene fragment); 57.07003 ((100%), C_4H_9, *tert*-butyl moiety).

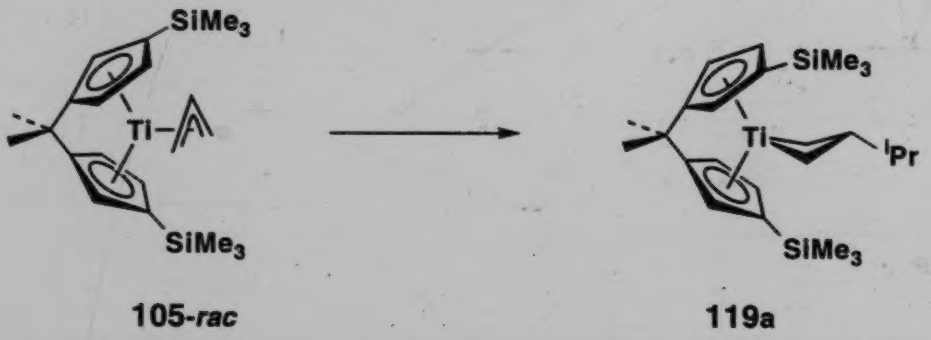
Titanacyclobutane 119a from Allyl Complex 105-*meso*::



105-*meso* **119a**

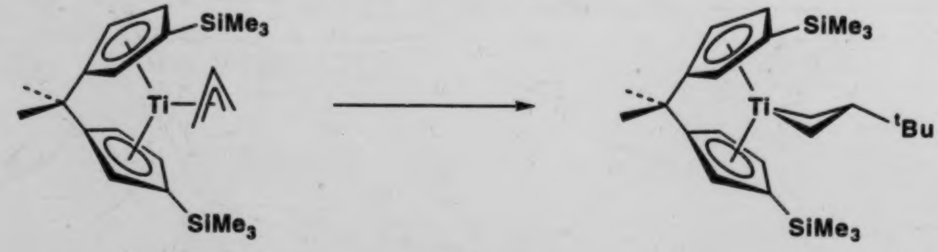
3-Isopropyl *meso ansa*-[1]-{dimethylmethano bis(3'-trimethylsilylcyclopentadienyl)} titanacyclobutane 119a. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of *meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium allyl **105-*meso*** (51.0 mg, 0.127 mmol) and SmI_2 (1.27 mL, 0.1 M in THF) was cooled to -35 °C. 2-Iodopropane (1 equivalent) was added *via* syringe to the cooled solution and the resulting reaction mixture was allowed to warm to room temperature and stirred for 6 h. The solvent was removed *in vacuo* to give a red-orange residue, which was triturated with pentane (10 mL) and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded red-brown micro rods (44.0 mg, 78%). Spectroscopic and high resolution mass spectrometry data for titanacyclobutane **119a**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 5.74 (t, *J* = 2.4 Hz, 1H, Cp), 5.62 (t, *J* = 2.4 Hz, 1H, Cp), 5.50 (t, *J* = 2.1 Hz, 1H, Cp), 5.44 (t, *J* = 2.5 Hz, 1H, Cp), 5.38 (t, *J* = 2.1 Hz, 1H, Cp), 5.35 (t, *J* = 2.5 Hz, 1H, Cp), 2.79 (t, *J* = 10.0, Hz, 1H, α-CH_2), 2.67 (t, *J* = 10.0 Hz, 1H, α-CH_2), 2.12 (t, *J* = 10.0 Hz, 1H, α-CH_2), 2.05 (t, *J* = 10.0 Hz, 1H, α-CH_2), 1.33 (s, 3H, $C(C\underline{H}_3)_2$), 1.16 (d, *J* = 6.4 Hz, 3H, $CH(C\underline{H}_3)_2$), 1.15 (t, *J* = 5.5 Hz, 2H, $CH(C\underline{H}_3)_2$), 1.15 (s, 3H, $C(C\underline{H}_3)_2$), 1.03 (m, 1H, $C\underline{H}(CH_3)_2$), 0.25 (s, 9H, $Si(C\underline{H}_3)_3$), 0.24 (s, 9H, $Si(C\underline{H}_3)_3$), -0.08 (m, 1H, β-CH). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 125.1 (s, Cp), 122.4 (s, Cp), 122.3 (d, *J* = 168.2 Hz, Cp), 122.1 (d, *J* = 170.4 Hz, Cp), 117.1 (s, Cp), 116.1 (s, Cp), 108.6 (d, *J* = 175 Hz, Cp), 108.6 (d, *J* = 175 Hz, Cp), 108.3 (d, *J* = 167.4 Hz, Cp), 106.9 (d, *J* = 169.7 Hz, Cp), 79.2 (t, *J* = 138.5 Hz, α-CH_2), 72.7 (t, *J* = 135.4 Hz, α-CH_2), 37.8 (d, *J* = 129.3 Hz, $\underline{C}H(CH_3)_2$), 36.0 (s, $\underline{C}(CH_3)_2$), 24.9 (q, *J* = 127.1 Hz, $C(\underline{C}H_3)_2$), 24.0 (q, *J* = 23.2 Hz, $\underline{C}(CH_3)_2$), 23.2 (q, *J* = 125.4 Hz, $CH(\underline{C}H_3)_2$), 22.6 (q, *J* = 125.4 Hz, $CH(\underline{C}H_3)_2$), 16.1 (d, *J* = 127.9 Hz, β-CH), -0.38 (q, *J* = 119.4 Hz, $Si(\underline{C}H_3)_3$), -0.71 (q, *J* = 118.9 Hz, $Si(\underline{C}H_3)_3$). IR (cm^{-1}, KBr, cast): 2951 (m), 2897 (w), 2870 (w), 1384 (w), 1370 (w), 1248 (s), 1175 (m), 1154 (w), 1092 (w), 1059 (w), 924 (w), 834 (vs), 754 (m), 736 (m), 692 (w), 668 (w), 632 (w), 615 (w). MS Calcd for $C_{25}H_{42}Si_2Ti$ *m/e* 446.23045, found 446.22484. Other important fragment ions include 362.13693 ((100%), $C_{19}H_{30}Si_2Ti$, titanocene template), and 84.09391 (4%), C_6H_{12}, hydrocarbon fragment of the titanacyclobutane moiety).

Titanacyclobutane 119a from Allyl Complex 105-*rac*:



3-Isopropyl *meso ansa*-[1]-{dimethylmethano bis(3'-trimethylsilylcyclopentadienyl)} titanacyclobutane 119a. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of *rac* *ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium allyl **105-*rac*** (79.0 mg, 0.196 mmol) and SmI_2 (1.96 mL, 0.1 M in THF) was cooled to -35 °C. 2-Iodopropane (1 equivalent) was added *via* syringe to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 6 h. The solvent was removed *in vacuo* to give a red-orange residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded red-brown micro rods (70.0 mg, 80%). Spectroscopic and high resolution mass spectrometry data for titanacyclobutane **119a** are identical in every respect to that previously prepared from allyl complex **105-*meso***.

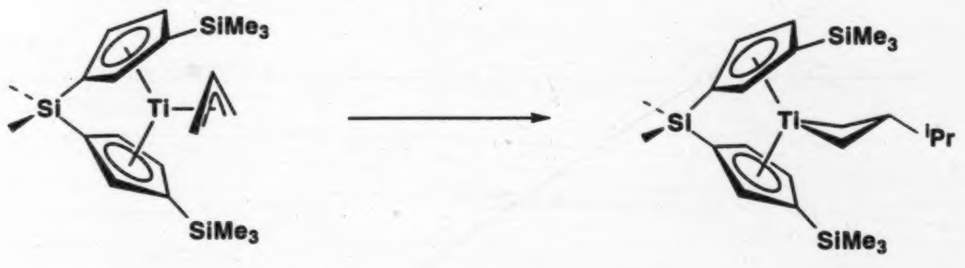
Titanacyclobutane 119b from Allyl Complex 105-*meso*:



105-*meso* **119b**

3-*tert*-Butyl *meso ansa*-[1]-{dimethylmethano bis(3'-trimethylsilylcyclopentadienyl)} titanacyclobutane 119b. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of *meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium allyl **105-*meso*** (56.0 mg, 0.161 mmol) and SmI_2 (1.61 mL, 0.1 M in THF) was cooled to -35 °C. 2-Chloro-2-methylpropane (1 equivalent) was added *via* syringe to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 6 h. The solvent was removed *in vacuo* to give a red-orange residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded red-brown micro rods (60.0 mg, 81%). Spectroscopic and high resolution mass spectrometry data for titanacyclobutane **119b**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 5.94 (t, J = 2.4 Hz, 1H, Cp), 5.83 (t, J = 2.5 Hz, 1H, Cp), 5.52 (t, J = 2.2 Hz, 1H, Cp), 5.35 (t, J = 2.5 Hz, 1H, Cp), 5.34 (t, J = 2.2 Hz, 1H, Cp), 5.29 (t, J = 2.5 Hz, 1H, Cp), 2.39 (t, J = 10.0 Hz, 1H, α-CH_2), 2.15 (t, J = 10.0 Hz, 1H, α-CH_2), 2.06 (t, J = 10.0 Hz, 1H, α-CH_2), 2.02 (t, J = 10.0 Hz, 1H, α-CH_2), 1.33 (s, 3H, $C(C\underline{H}_3)_2$), 1.10 (s, 3H, $C(C\underline{H}_3)_2$), 1.00 (s, $C(C\underline{H}_3)_3$), 0.26 (s, 9H, $Si(C\underline{H}_3)_3$), 0.25 (s, 9H, $Si(C\underline{H}_3)_3$), 0.17 (m, 1H, β-CH). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 125.8 (s, Cp), 122.7 (d, J = 170.3 Hz, Cp), 122.3 (s, Cp), 121.3 (d, J = 170.3 Hz, Cp), 117.6 (s, Cp), 116.6 (s, Cp), 109.7 (d, J = 166.8 Hz, Cp), 109.5 (d, J = 170.3 Hz, Cp), 108.3 (d, J = 167.5 Hz, Cp), 107.4 (d, J = 170.3 Hz, Cp), 72.1 (t, J = 139.4 Hz, α-CH_2), 65.5 (t, J = 134.6 Hz, α-CH_2), 35.9 (s, $\underline{C}(CH_3)_2$), 34.3 (s, $\underline{C}(CH_3)_3$), 29.2 (q, J = 124.3 Hz, $C(\underline{C}H_3)_3$), 25.1 (q, J = 128.4 Hz, $C(\underline{C}H_3)_2$), 22.5 (q, J = 128.4 Hz, $C(\underline{C}H_3)_2$), 20.3 (d, J = 127.9 Hz, β-CH), -0.15 (d, J = 119.1 Hz, $Si(\underline{C}H_3)_3$), -0.65 (d, J = 118.9 Hz, $Si(\underline{C}H_3)_3$). ^1H-^1H correlations (400.1 MHz, C_6D_6): δ 5.94 ↔ 5.52, 5.35; 5.83 ↔ 5.34, 5.29; 2.39 ↔ 2.02, 0.17; 2.15 ↔ 2.06, 0.17. ^{13}C-^1H correlations (400.1 MHz, C_6D_6): δ 122.7 ↔ 5.83; 121.3 ↔ 5.94; 109.7 ↔ 5.52; 109.5 ↔ 5.29; 108.3 ↔ 5.34; 107.4 ↔ 5.35; 72.1 ↔ 2.39, 2.02; 65.5 ↔ 2.15, 2.06; 29.2 ↔ 1.00; 25.1 ↔ 1.33, 22.5 ↔ 1.10; 20.3 ↔ 0.17. IR (cm^{-1}, KBr, cast): 2949 (m), 2897 (w), 1370 (w), 1356 (w), 1246 (m), 1175 (m), 1164 (w), 1154 (w), 1095 (w), 1082 (w), 1058 (w), 925 (w), 833 (vs), 801 (m), 754 (m), 736 (m), 718 (w), 690 (w). MS Calcd for $C_{26}H_{44}Si_2Ti$ *m/e* 460.24611. No molecular ion was observed, however, important fragment ions that support the elemental composition of complex **119b** include: *m/e* 376.15345 ((14%), $C_{19}H_{30}Si_2Ti$, the titanium methylidene fragment), 362.13886 ((100%), $C_{19}H_{30}Si_2Ti$, titanocene template), 84.09267 ((4%), C_6H_{12}, 2,2-dimethylbutene fragment).

Titanacyclobutane 120a from Allyl Complex 108-*meso*:

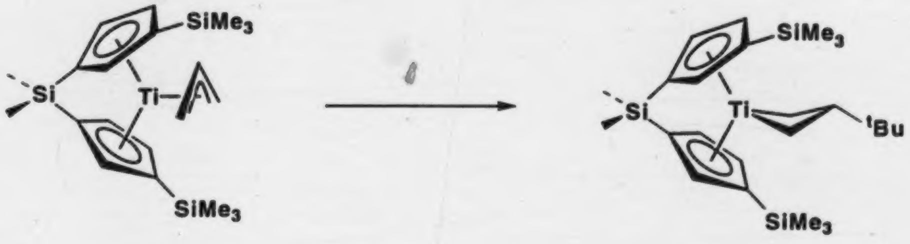


108-*meso*

120a

3-Isopropyl *meso ansa*-[1]-{dimethylsilylbis(3'-trimethylsilylcyclopentadienyl)}-titanacyclobutane 120a. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of *meso ansa*-[1]-{dimethylsilyl bis(3-trimethylsilylcyclopentadienyl)}titanium allyl **108-*meso*** (63.0 mg, 0.150 mmol) and SmI$_2$ (1.5 mL, 0.1 M in THF) was cooled to -35 °C. 2-Iodopropane (1 equivalent) was added *via* syringe to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 6 h. The solvent was removed *in vacuo* to give a red-orange residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded red-brown micro rods (66.0 mg, 95%). Spectroscopic and high resolution mass spectrometry data for titanacyclobutane **120a**: ^{1}H NMR (400.1 MHz, C$_6$D$_6$): δ 5.96 (brs, 1H, Cp), 5.84 (brs, 3H, Cp), 5.67 (brs, 1H, Cp), 5.51 (brs, 1H, Cp), 2.77 (t, J = 10.0 Hz, 1H, α-CH$_2$), 2.57 (t, J = 10.0 Hz, 1H, α-CH$_2$), 2.22 (t, J = 10.0 Hz, 1H, α-CH$_2$), 2.09 (t, J = 10.0 Hz, 1H, α-CH$_2$), 1.13 (d, J = 6.3 Hz, 3H, CH(C$\underline{\mathrm{H}}_3$)$_2$), 1.10 (d, J = 6.4 Hz, 3H, CH(C$\underline{\mathrm{H}}_3$)$_2$), 0.88 (m, 1H, C$\underline{\mathrm{H}}$(CH$_3$)$_2$), 0.32 (s, 3H, Si(C$\underline{\mathrm{H}}_3$)$_2$), 0.26 (s, 9H, Si(C$\underline{\mathrm{H}}_3$)$_3$), 0.25 (s, 9H, Si(C$\underline{\mathrm{H}}_3$)$_3$), 0.17 (s, 3H, Si(C$\underline{\mathrm{H}}_3$)$_2$), -0.24 (m, 1H, β-CH). ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$, APT): δ 131.7 (Cp$_{\mathrm{quaternary}}$), 128.7 (Cp$_{\mathrm{quaternary}}$), 125.6 Cp$_{\mathrm{methine}}$), 125.2 Cp$_{\mathrm{methine}}$), 118.4 (Cp$_{\mathrm{quaternary}}$), 117.1 Cp$_{\mathrm{methine}}$), 116.6 Cp$_{\mathrm{methine}}$), 114.5 Cp$_{\mathrm{methine}}$), 112.6 Cp$_{\mathrm{methine}}$), 105.3 (Cp$_{\mathrm{quaternary}}$), 78.2 (α-CH$_2$), 70.6 (α-CH$_2$), 38.1 ($\underline{\mathrm{C}}$H(CH$_3$)$_2$), 23.9 (CH($\underline{\mathrm{C}}$H$_3$)$_2$), 23.2 (CH($\underline{\mathrm{C}}$H$_3$)$_2$), 13.6 (β-CH), 0.11 (Si($\underline{\mathrm{C}}$H$_3$)$_3$), -0.33 (Si($\underline{\mathrm{C}}$H$_3$)$_3$), -3.6 (Si($\underline{\mathrm{C}}$H$_3$)$_2$), -6.5 (Si($\underline{\mathrm{C}}$H$_3$)$_2$). IR (cm^{-1}, KBr, cast): 3082 (w), 2953 (m), 2897 (w), 1509 (w), 1445 (w), 1406 (w), 1384 w), 1248 (s), 1209 (w), 1180 (w), 1171 (w), 1442 (w), 1087 (s), 1056 (w), 924 (w), 891 (w), 833 (vs), 802 (s), 785 (m), 754 (m), 692 (w), 671 (w), 634 (w), 482 (w), 472 (w). MS Calcd for C$_{24}$H$_{42}$Si$_3$Ti *m/e* 462.20738. No molecular ion was observed, however, fragment ions supporting the elemental composition of complex **120a** include: *m/e* 392.12843 ((3%), (C$_{19}$H$_{32}$Si$_3$Ti, the titanocene methylidene fragment), 378.11395 ((96%), C$_{18}$H$_{30}$Si$_3$Ti, the titanocene template); 84.09356 ((7%), C$_6$H$_{12}$, the hydrocarbon moiety of the titanacyclobutane); 70.0778 ((10%), C_5H_{10}, 2-methylbutene fragment, complimentary to the titanocene methylidene fragment).

Titanacyclobutane 120b from Allyl Complex 108-*meso*:

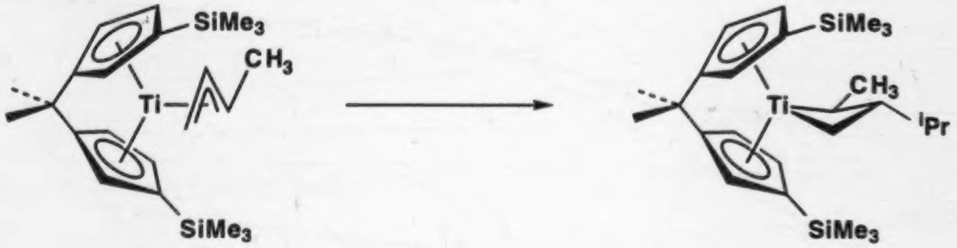


108-*meso* **120b**

3-*tert*-Butyl *meso ansa*-[1]-{dimethylsilylbis(3'-trimethylsilylcyclopentadienyl)}-titanacyclobutane 120b. In the drybox, a 25 mL round flask containing a THF solution (10 mL) of *meso ansa*-[1]-{dimethylsilyl bis(3-trimethylsilylcyclopentadienyl)}titanium allyl **108-*meso*** (63.0 mg, 0.150 mmol) and SmI_2 (1.5 mL, 0.1 M in THF) was cooled to -35 °C. 2-Chloro-2-methylpropane (1 equivalent) was added *via* syringe to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 6 h. The solvent was removed *in vacuo* to give a red-orange residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded red-brown micro rods (60.0 mg, 83%). Spectroscopic and high resolution mass spectrometry data for titanacyclobutane **120b**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 6.20 (t *J* = 2.0 Hz, 1H, Cp), 6.13 (t, *J* = 2.0 Hz, 1H, Cp), 5.91 (t *J* = 2.0 Hz, 1H, Cp), 5.82 (t, *J* = 2.0 Hz, 1H, Cp), 5.69 (t, *J* = 2.0 Hz, 1H, Cp), 5.48 (t, *J* = 2.0 Hz, 1H, Cp), 2.34 (t, *J* = 10.0 Hz, 1H, α-CH_2), 2.12 (t, *J* = 10.0 Hz, 1H, α-CH_2), 2.06 (t, *J* = 10.0 Hz, 1H, α-CH_2), 2.00 (t, *J* = 10.0 Hz, 1H, α-CH_2), 0.97 (s, 9H, $C(C\underline{H}_3)_3$)), 0.32 (s, 3H, $Si(C\underline{H}_3)_2$), 0.26 (s, 9H, $Si(C\underline{H}_3)_3$), 0.24

(s, 9H, $Si(C\underline{H}_3)_3$), 0.14 (s, 3H, $Si(C\underline{H}_3)_2$), 0.05 (quintet, *J* = 10.0 Hz, 1H, β-CH). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 132.0 (s, Cp) , 128.6 (s, Cp), 126.0 (d, *J* = 166.0 Hz, Cp), 124.4 (d, *J* = 166.8 Hz, Cp), 118.0 (d, *J* = 171.5 Hz, Cp), 117.4 (d, *J* = 164.3 Hz, Cp), 115.8 (d, *J* = 166.8 Hz, Cp), 112.8 (d, *J* = 167.1 Hz, Cp), 105.7 (s, Cp), 105.6 (s, Cp), 70.5 (t, *J* = 139.0 Hz, α-CH_2), 63.6 (t, *J* = 136.0 Hz, α-CH_2), 34.1 (s, $\underline{C}(CH_3)_3$), 29.0 (q, *J* = 123.5 Hz, $C(\underline{C}H_3)_3$), 18.1 (d, *J* = 128.0 Hz, β-CH), 0.3 (q, *J* = 119.0 Hz, $Si(\underline{C}H_3)_3$), -0.3 (q, *J* = 119.0 Hz, $Si(\underline{C}H_3)_3$), -3.5 (q, *J* = 119.7 Hz, $Si(\underline{C}H_3)_2$), -6.6 (q, *J* = 119.1 Hz, $Si(\underline{C}H_3)_2$). IR (cm^{-1}, KBr, cast): 2955 (vs), 2899 (m), 2872 (w), 2859 (w), 1448 (w), 1406 (w), 1248 (vs), 1211(w), 1085 (vs), 1053 (w), 923 (s), 836 (vs), 787 (s), 755 (s), 694 (w), 671 (s), 634 (w), 483 (w), 471 (w). MS Calcd for $C_{25}H_{44}Si_3Ti$ *m/e* 476.22303, found 476.22302.

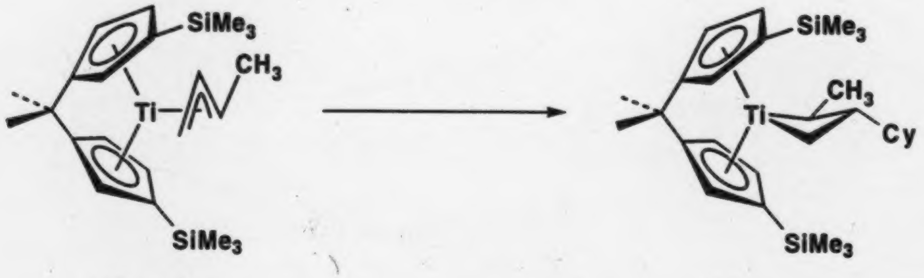
Titanacyclobutane 121a from Crotyl Complex 106-*meso*:



106-*meso* **121a**

3-Isopropyl-2-methyl *meso ansa*-[1]-{dimethylmethano bis(3'-trimethylsilylcyclopentadienyl)}titanacyclobutane 121a. In the drybox, a 50 mL round bottom flask containing a THF solution (30 mL) of *meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium crotyl **106-*meso*** (224.7 mg, 0.538 mmol) and SmI_2 (5.38 mL, 0.1 M in THF) was cooled to -35 °C. 2-Iodopropane (1 equivalent) was added *via* syringe to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 4 h The solvent was removed *in vacuo* to give a red-orange residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded red-brown micro rods (236 mg, 95%). Spectroscopic and analytical data for titanacyclobutane **121a**: ^{1}H NMR (200.1 MHz, C_6D_6): δ 6.00 (t, *J* = 2.4 Hz, 1H, Cp), 5.68 (t, *J* = 2.5, 1H, Cp), 5.47 (t, *J* = 2.1, 1H, Cp), 5.36 (t, *J* = 2.4, 1H, Cp), 5.34 (t, *J* = 2.5, 1H, Cp), 4.99 (t, *J* = 2.5, 1H, Cp), 2.65 (dq, *J* = 10.0, 6.9, 1H, α-$\mathrm{C\underline{H}(CH_3)}$), 2.40 (t, *J* = 10.0, 1H, α-$\mathrm{C\underline{H}_2}$), 2.14 (t, *J* = 10.0, 1H, α-$\mathrm{C\underline{H}_2}$), 1.80 (m, 1H, $\mathrm{C\underline{H}(CH_3)_2}$), 1.65 (d, *J* = 6.9, 3H, α-$\mathrm{CH(C\underline{H}_3)}$), 1.37 (s, 3H, $\mathrm{C(C\underline{H}_3)_2}$), 1.15 (s, 3H, $\mathrm{C(C\underline{H}_3)_2}$), 1.12 (d, *J* = 6.7, 3H, $\mathrm{CH(C\underline{H}_3)_2}$), 0.83 (d, *J* = 6.7, 3H, $\mathrm{CH(C\underline{H}_3)_2}$), 0.25 (s, 9H, $\mathrm{Si(C\underline{H}_3)_3}$), 0.24 (s, 9H, $\mathrm{Si(C\underline{H}_3)_3}$), -0.27 (m, 1H, β-CH). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 125.3 (s, Cp), 123.3 (s, Cp), 122.6 (d, *J* = 165.6 Hz, Cp), 118.0 (d, *J* = 161.9 Hz, Cp), 117.4 (s, Cp), 117.3 (s, Cp), 110.9 (d, *J* = 169.9 Hz, Cp), 110.4 (d, *J* = 159.1 Hz, Cp), 108.3 (d, *J* = 166.6 Hz, Cp), 106.2 (d, *J* = 169.8 Hz, Cp), 89.5 (d, *J* = 132.2 Hz, α-$\mathrm{\underline{C}H(CH_3)}$), 66.6 (t, *J* = 134.9 Hz, α-$\mathrm{\underline{C}H_2}$), 35.9 (s, $\mathrm{\underline{C}(CH_3)_2}$), 30.9 (d, *J* = 128.1 Hz, $\mathrm{\underline{C}H(CH_3)_2}$), 26.8 (q, *J* = 122.3 Hz, α-$\mathrm{CH(\underline{C}H_3)}$), 25.3 (q, *J* = 125.7 Hz, $\mathrm{C(\underline{C}H_3)_2}$), 23.8 (q, *J* = 125.0 Hz, β-CH), 22.8 (q, *J* = 127.6 Hz, $\mathrm{CH(\underline{C}H_3)_2}$), 22.5 (q, *J* = 127.6 Hz, $\mathrm{CH(\underline{C}H_3)_2}$), 18.8 (q, *J* = 119.9 Hz, $\mathrm{C(\underline{C}H_3)_2}$), -0.2 (q, *J* = 118.9 Hz, $\mathrm{Si(\underline{C}H_3)_3}$), -0.6 (q, *J* = 119.1 Hz, $\mathrm{Si(\underline{C}H_3)_3}$). IR (cm^{-1}, KBr, cast): 2952 s, 2869 (m), 1369 (w), 1247 (s), 1175 (m), 1154 (m), 1091 (m), 1058 w, 925 (m), 835 (vs), 754 (m), 734 (m), 690 (w), 632 (w). Anal Calcd for $C_{26}H_{44}Si_2Ti$: C, 67.79 H, 9.63. Found C, 67.88; H, 9.36.

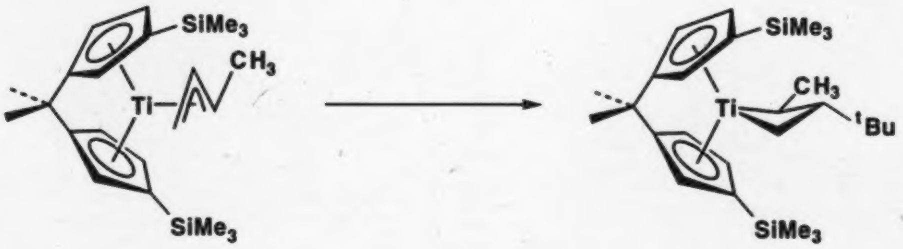
Titanacyclobutane 121b from Crotyl Complex 106-*meso*:



106-*meso* **121b**

3-Cyclohexyl-2-methyl *meso ansa*-[1]-{dimethylmethano bis(3'-trimethylsilylcyclopentadienyl)}titanacyclobutane 121b. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of *meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium crotyl **106-*meso*** (34.0 mg, 0.0941 mmol) and SmI_2 (0.94 mL, 0.1 M in THF) was cooled to -35 °C. Cyclohexyl iodide (1 equivalent) was added *via* syringe to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 40 minutes. The solvent was removed *in vacuo* to give a red-orange residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded red-brown micro rods (46.0 mg, 97%). Spectroscopic and high resolution mass spectrometry data for titanacyclobutane **121b**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 5.98 (t, J = 2.2 Hz, 1H, Cp), 5.64 (t, J = 2.2 Hz, 1H, Cp), 5.47 (t, J = 2.1, 1H, Cp), 5.38 (t, J = 2.6 Hz, 1H, Cp), 5.37 (t, J = 2.6 Hz, 1H, Cp), 5.01 (t, J = 2.3 Hz, 1H, Cp), 2.73 (dq, J = 10.0, 6.9 Hz, 1H, $\alpha\text{-C}\underline{\text{H}}(\text{CH}_3)$), 2.52 (t, J = 10.0 Hz, 1H, $\alpha\text{-CH}_2$), 2.20 (t, J = 10.0 Hz, 1H, $\alpha\text{-CH}_2$), 1.77 (m, 4H, $\text{C}\underline{\text{H}}_2(\text{cy})$), 1.67 (d, J = 6.9 Hz, 3H, $\alpha\text{-CH}(\text{C}\underline{\text{H}}_3)$), 1.37 (s, 3H, $\text{C}(\text{C}\underline{\text{H}}_3)_2$), 1.31 (m, 6H, $\text{C}\underline{\text{H}}_2(\text{cy})$), 1.17 (s, 3H, $\text{C}(\text{C}\underline{\text{H}}_3)_2$), 0.99 (m, 1H, $\text{C}\underline{\text{H}}(\text{cy})$), 0.26 (s, 9H, $\text{Si}(\text{C}\underline{\text{H}}_3)_3$), 0.25 (s, 9H, $\text{Si}(\text{C}\underline{\text{H}}_3)_3$), -0.33 (m, 1H, β-CH). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 125.2 (s, Cp), 123.5 (s, Cp), 122.8 (d, J = 166.1 Hz, Cp), 117.8 (d, J = 169.9 Hz, Cp), 117.5 (s, Cp), 117.4 (s, Cp), 111.0 (d, J = 169.7 Hz, Cp), 110.4 (d, J = 166.8 Hz, Cp), 108.1 (d, J = 191.8 Hz, Cp), 106.2 (d, J = 195.6 Hz, Cp), 89.2 (d, J = 127.4 Hz, α-$\underline{\mathrm{C}}\mathrm{H(CH_3)}$), 69.6 (t, J = 135.4 Hz, α-$\mathrm{CH_2}$), 43.2 (d, J = 125.6 Hz, $\underline{\mathrm{C}}$H(cy)), 36.0 (s, $\underline{\mathrm{C}}\mathrm{(CH_3)_2}$), 35.0 (t, J = 122.1 Hz, $\underline{\mathrm{C}}\mathrm{H_2}$(cy)), 30.5 (t, J = 128.8 Hz, $\underline{\mathrm{C}}\mathrm{H_2}$(cy)), 28.0 (t, J = 124.0 Hz, $\underline{\mathrm{C}}\mathrm{H_2}$(cy)), 27.6 (t, J = 122.1 Hz, $\underline{\mathrm{C}}\mathrm{H_2}$(cy)), 27.5 (t, J = 122.1 Hz, $\underline{\mathrm{C}}\mathrm{H_2}$(cy)), 27.4 (q, J = 122.4 Hz, α-$\mathrm{CH(\underline{C}H_3)}$), 25.2 (q, J = 126.0 Hz, $\mathrm{C(\underline{C}H_3)_2}$), 22.6 (q, J = 130.0 Hz, β-CH), 22.1 (q, J = 122.1 Hz, $\mathrm{C(\underline{C}H_3)_2}$), -0.2 (q, J = 118.5 Hz, $\mathrm{Si(\underline{C}H_3)_3}$), -0.6 (q, J = 118.6 Hz, $\mathrm{Si(\underline{C}H_3)_3}$). IR (cm^{-1}, KBr, cast): 2950 (s), 2922 (s), 2871 (m), 2850 (s), 1447 (m), 1404 (m), 1385 (m), 1370 (m), 1248 (s), 1176 (m), 1153 (m), 1095 (m), 1082 (m), 1060 (m), 928 (m), 833 (vs), 754 (s), 735 (m), 692 (m), 632 (m). MS Calcd for $\mathrm{C_{29}H_{48}Si_2Ti}$ *m/e* 500.27741, found 500.27014. Other important ions include: *m/e* 362.13514 ((100), titanocene template, $\mathrm{C_{19}H_{30}Si_2Ti}$); 138.14076 ((4%), $\mathrm{C_{10}H_{18}}$, hydrocarbon fragment of titanacyclobutane).

Titanacyclobutane 121c from Crotyl Complex 106-*meso*:

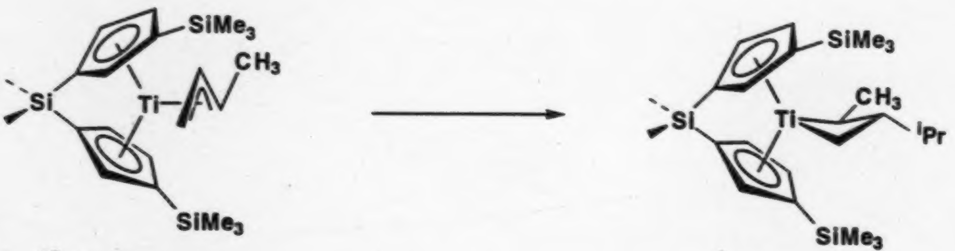


106-*meso* **121c**

3-*tert*-Butyl-2-methyl *meso ansa*-[1]-{dimethylmethano bis(3'-trimethylsilylcyclopentadienyl)}titanacyclobutane 121c. In the drybox, a 50 mL round bottom flask containing a THF solution (30 mL) of *meso ansa*-[1]-{dimethylmethano bis(3-

trimethylsilylcyclopentadienyl)}titanium crotyl **106-*meso*** (224.7 mg, 0.538 mmol) and SmI_2 (5.38 mL, 0.1 M in THF) was cooled to -35 °C. 2-Chloro-2-methylpropane (1 equivalent) was added *via* syringe to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 4 h. The solvent was removed *in vacuo* to give a red-orange residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded red-brown micro rods (211 mg, 81%). Spectroscopic (^{1}H NMR only) data for titanacyclobutane **121c**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 6.31 (brs, 1H, Cp), 6.02 (brs, 1H, Cp), 5.47 (brs, 1H, Cp), 5.33 (brs, 1H, Cp), 5.24 (brs, 1H, Cp), 4.35 (brs, 1H, Cp), 2.49 (m, 1H, α-$C\underline{H}(CH_3)$), 2.30 (t, J = 10.0 Hz, 1H, α-CH_2), 2.21 (t, J = 10.0 Hz, 1H, α-CH_2), 1.65 (d, J = 6.8 Hz, 3H, α-$CH(C\underline{H}_3)$), 1.36 (s, 3H, $C(C\underline{H}_3)_2$), 1.12 (s, 3H, $C(C\underline{H}_3)_2$), 1.01 (s, 9H, $C(C\underline{H}_3)_3$), 0.25 (s, 9H, $Si(C\underline{H}_3)_3$), 0.24 (s, 9H, $Si(C\underline{H}_3)_3$), -0.03 (m, 1H, β-CH).

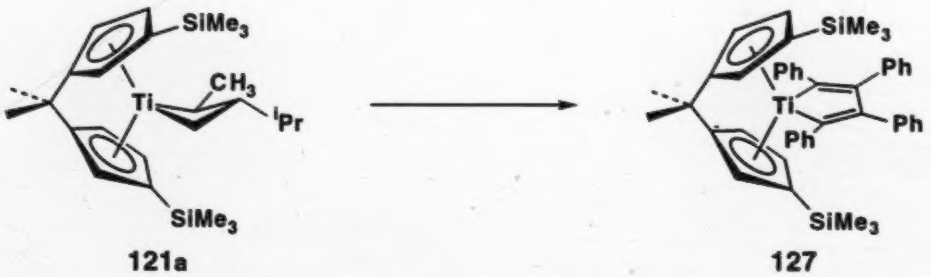
Titanacyclobutane 122a from Crotyl Complex 104-*meso*:



7 **104-*meso*** **122a**

3-Isopropyl-2-methyl *meso ansa*-[1]-{dimethylsilylbis(3'-trimethylsilylcyclopentadienyl)}titanacyclobutane 122a. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of *meso ansa*-[1]-{dimethylsilyl bis(3-trimethylsilylcyclopentadienyl)}titanium crotyl **104-*meso*** (225 mg, 0.538 mmol) and SmI_2 (5.38 mL, 0.1 M in THF) was cooled to -35 °C. 2-Iodopropane (1 equivalent) was added *via* syringe to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 4 h. The solvent was removed *in vacuo* to give a red-orange residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded red-brown micro rods (56.0 mg, 65%). Spectroscopic (^{1}H NMR and infrared) and high resolution mass spectrometry data for titanacyclobutane **122a**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 6.18 (brs, 1H, Cp), 5.86 (brs, 2H, Cp), 5.65 (brs, 1H, Cp), 5.56 (brs, 1H, Cp), 5.50 (brs, 1H, Cp), 2.76 (m, 1H, α-$C\underline{H}(CH_3)$), 2.45 (t, J = 10.0 Hz, 1H, α-CH_2), 2.31 (t, J = 10.0 Hz, 1H, α-CH_2), 1.69 (d, J = 6.9 Hz, 3H, α-$CH(C\underline{H}_3)$), 1.08 (d, J = 6.5 Hz, 3H, $CH(C\underline{H}_3)_2$), 0.84 (d, J = 6.6 Hz, 3H, $CH(C\underline{H}_3)_2$), 0.35 (s, 3H, $Si(C\underline{H}_3)_2$), 0.26 (s, 9H, $Si(C\underline{H}_3)_3$), 0.24 (s, 9H, $Si(C\underline{H}_3)_3$), 0.18 (s, 3H, $Si(C\underline{H}_3)_2$), -0.31 (m, 1H, β-CH). IR (cm^{-1}, KBr, cast): 2954 (s), 2924 (m), 2897 (m), 2874 (m), 2852 (m), 1444 (m), 1405 (m), 1266 (s), 1247 (vs), 1208 (m), 1087 (vs), 1053 (m), 925 (s), 881 (m), 834 (vs), 803 (s), 785 (s), 755 (s), 734 (m), 692 (m), 671 (s), 634 (m), 483 (m), 474 (m). MS Calcd for $C_{25}H_{44}Si_3Ti$ *m/e* 476.22303. No molecular ion was observed, however, important fragment ions that lend support to the elemental composition of complex **122a** include: *m/e* 378.11347 ((41%), $C_{18}H_{30}Si_3Ti$, the titanocene template); 98.10933 ((3%), C_7H_{14}, the hydrocarbon moiety of the titanacyclobutane).

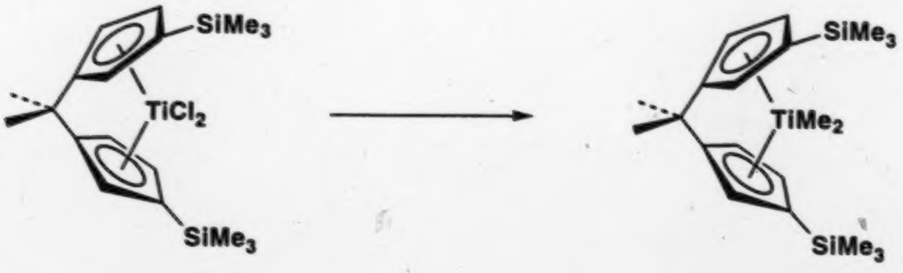
Titanacyclopentadiene 127 from *meso*-Titanacyclobutane Complex 121a:



***meso* 2,3,4,5-Tetraphenyl *ansa*-[1]-{dimethylmethano bis(3'-trimethylsilylcyclopentadienyl)}titanacyclopentadiene 127**. In the drybox, a benzene-d_6 solution of 3-isopropyl-2-methyl *meso* *ansa*-[1]-{dimethylmethano bis(3'-trimethylsilylcyclopentadienyl)}titanacyclobutane **121a** (25.0 mg, 0.0543 mmol) and diphenylacetylene (10.0 mg, 0.0543 mmol) was placed in a Teflon-capped re-sealable NMR tube at room temperature. The reaction mixture was allowed to stand at room temperature for 18 h. Subsequently, the NMR tube was taken out of the drybox and the volatile fraction was vacuum-transferred into another Teflon-capped re-sealable NMR tube. The resulting residue was taken into the drybox and recrystallized from hexane at -35 °C to afford yellow-brown needles (30.0 mg, 77%). Spectroscopic and high resolution mass spectrometry data for complex **127**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 7.92 (t, J = 2.3 Hz, 2H, Cp), 7.13 (m, J = 1.4, 8.4 Hz, 2H, $C_6\underline{H}_5$), 6.86 (m, 14H, $C_6\underline{H}_5$), 6.07 (d, J = 8.6 Hz, 2H, $C_6\underline{H}_5$), 5.50 (t, J = 2.1 Hz, 2H, Cp), 4.65 (t, J = 2.6 Hz, 2H, Cp), 1.24 (s, 3H, $C(C\underline{H}_3)_2$), 1.09 (s, 3H, $C(C\underline{H}_3)_2$), 0.30 (s, 18H, $Si(C\underline{H}_3)_3$). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 206.1 (s), 194.7 (s), 150.4 (s), 146.8 (s), 142.8 (s), 141.5 (s), 139.8 (s), 134.5 (s), 131.9 (C_{methine}), 131.5 (C_{methine}), 131.2 (C_{methine}), 131.1 (C_{methine}), 129.3 (C_{methine}), 128.65 (C_{methine}), 127.2 (C_{methine}), 126.8 (C_{methine}), 125.5 (C_{methine}), 124.6 (C_{methine}), 124.5 (C_{methine}), 123.9 (C_{methine}), 123.6 (C_{methine}), 117.2 (s, Cp), 115.6 (d, J = 169.4 Hz, Cp), 114.7 (d, J = 168.4 Hz, Cp), 109.3 (s, Cp), 36.6 (s, $\underline{C}(CH_3)_2$), 24.3 (q, J = 125 Hz,

$C(\underline{C}H_3)_2$), 22.5 (q, *J* = 125 Hz, $C(\underline{C}H_3)_2$), -0.17 (q, *J* = 119.3 Hz, $Si(\underline{C}H_3)_3$). To avoid overlapping of the solvent signal with signals for complex **127**, ^1H and ^{13}C NMR spectra were acquired in cyclohexane-*d*$_6$. ^1H NMR (400.1 MHz, C_6D_{12}): δ 7.73 (t, *J* = 2.1, 2H, Cp), 7.19 (m, 2H), 6.86 (dd, *J* = 7.8, 7.6, 2H, $C_6\underline{H}_5$), 6.77 (m, 3H, $C_6\underline{H}_5$), 6.69 (m, 5H, $C_6\underline{H}_5$), 6.54 (m, 3H, $C_6\underline{H}_5$), 6.44 (m, 3H, $C_6\underline{H}_5$), 5.80 (d, *J* = 6.9, 2H, $C_6\underline{H}_5$), 5.45 (dd, *J* = 2.1, 2H, Cp), 4.60 (dd, *J* = 2.5, 2H, Cp), 1.59 (s, 3H, $C(C\underline{H}_3)_2$), 1.49 (s, 3H, $C(C\underline{H}_3)_2$), 0.09 (s, 18H, $Si(C\underline{H}_3)_3$). ^{13}C NMR (100.6 MHz, C_6D_{12}, gated decoupled): δ 206.3 (s), 192.8 (s), 150.6 (s), 147.1 (s), 142.8 (s), 141.5 (s), 140.1 (s), 134.8 (s), 131.7 ($C_{methine}$), 131.6 ($C_{methine}$), 131.4 ($C_{methine}$), 129.7 ($C_{methine}$), 128.4 (s), 127.8 ($C_{methine}$), 127.5 ($C_{methine}$), 127.4 ($C_{methine}$), 126.9 ($C_{methine}$), 126.6 ($C_{methine}$), 125.3 ($C_{methine}$), 124.6 ($C_{methine}$), 124.5 ($C_{methine}$), 123.6 ($C_{methine}$), 117.3 (s, Cp), 115.8 (d, *J* = 168.7 Hz, Cp), 114.8 (d, *J* = 168.0 Hz, Cp), 37.2 (s, $\underline{C}(CH_3)_2$), 25.1 (q, *J* = 134 Hz, $C(\underline{C}H_3)_2$), 23.1 (q = 126.8 Hz, $C(\underline{C}H_3)_2$), -0.15 (q, *J* = 119.3 Hz, $Si(\underline{C}H_3)_3$). IR (cm^{-1}, KBr, cast): 3081 (m), 3059 (m), 3033 (m), 3021 (m), 2955 (m), 2897 (m), 1601 (m), 1498 (m), 1443 (m), 1248 (s), 1174 (m), 1164 (m), 1087 (m), 1070 (m), 1027 (m), 917 (m), 839 (vs), 798 (m), 755 (vs), 690 (s), 671 (m), 664 (m), 630 (m), 536 (s). MS Calcd for $C_{47}H_{50}Si_2Ti$ *m/e* 718.29303, found 718.28949. Partial spectroscopic (^1H NMR only) data for **3,4-dimethyl-1-pentene 125**: ^1H NMR (C_6D_6, 400.1 MHz): δ 5.67 (m, 1H), 4.95 (m, 2H), 1.85 (m, 1H), 1.40 (m, 1H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 5.7 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H). GCMS (single ion [69] chromatography): *m/e* 84.1, 69.1, 41.

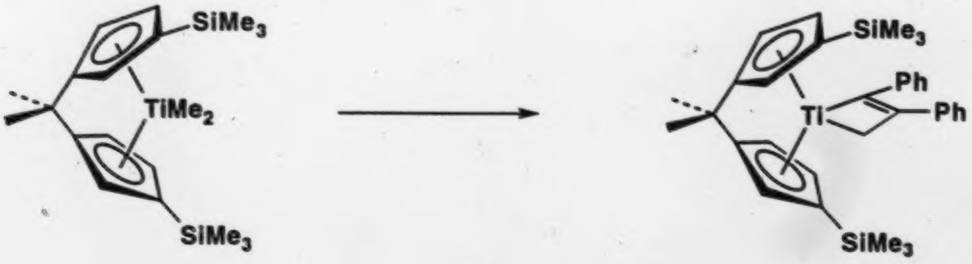
***Meso*-Titanocene Dimethyl Complex 128 from *meso*-Titanocene Dichloride 132:**



132-*meso* **128**

Meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium dimethyl complex 128**. To a hexane solution (5 mL) of *meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium dichloride **132-*meso (21.2 mg, 0.0489 mmol) in a 25 mL Schlenk flask at -78 °C was added methyllithium (100 µL, 1 M in diethyl ether). The cooling bath was then removed and the reaction mixture allowed to warm to room temperature and stirred for 1.5 h. The solvents were removed *in vacuo* and the yellow residue was triturated with hexane and the solution filtered through a short column of celite. Subsequent removal of the solvent yielded a yellow crystalline solid (18.0 mg, 93%), which was used without further purification. Partial spectroscopic data (^{1}H and ^{13}C NMR) for complex **128**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 7.02 (t, *J* = 2.4 Hz, 2H, Cp), 5.18 (t, *J* = 2.2 Hz, 2H, Cp), 4.97 (t, *J* = 2.6 Hz, 2H, Cp), 1.13 (s, 3H, $C(C\underline{H}_3)_2$), 1.01 (s, 3H, $C(C\underline{H}_3)_2$), 0.41 (s, 18H, $Si(C\underline{H}_3)_3$), 0.35 (s, 3H, Ti-$C\underline{H}_3$), 0.30 (s, 3H, Ti-$C\underline{H}_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, APT): δ 127.0 ($Cp_{quaternary}$)), 116.0 ($Cp_{quaternary}$), 112.7 ($Cp_{methine}$), 111.4 ($Cp_{methine}$), 111.4 ($Cp_{methine}$), 45.8 (Ti-$\underline{C}H_3$), 43.0 (Ti-$\underline{C}H_3$), 35.6 ($\underline{C}(CH_3)_2$), 24.7 ($C(\underline{C}H_3)_2$), 22.4 ($C(\underline{C}H_3)_2$), -0.19 ($Si(\underline{C}H_3)_3$).

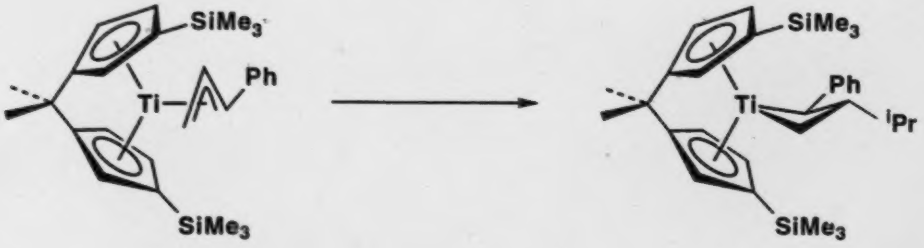
Titanacyclobutene 129 from *meso*-Titanocene Dimethyl Complex 128:



128 **129**

2,3-Diphenyl *meso* *ansa*-[1]-{dimethylmethano bis(3'-trimethylsilylcyclopentadienyl)}titanacyclobutene 129. In the drybox, a Teflon-capped NMR tube was charged with *meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium dimethyl complex **128** (18.0 mg, 0.0456 mmol), diphenylacetylene (8.1 mg) and benzene-d_6 (0.5 mL). The sealed tube was taken out of the drybox and heated to 80 °C for 37 h in an oil bath and during this time the color of the reaction mixture changed from yellow to brown. The mixture was allowed to cool to room temperature, taken into the drybox and the solvent subsequently removed *in vacuo*. The brown residue was recrystallized from hexane cooled to -35 °C affording brown micro-rods (23.0 mg, 90%). Spectroscopic and high resolution mass spectrometry data for complex **129**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 7.41 (dd, J = 8.0, 1.2 Hz, 2H, $C_6\underline{H}_5$), 7.21 (dd, J = 7.9, 7.6 Hz, 2H, $C_6\underline{H}_5$), 7.00 (m, 6H, $C_6\underline{H}_5$), 6.45 (t, J = 2.4 Hz, 2H, Cp), 5.59 (t, J = 2.2 Hz, 2H, Cp), 5.29 (t, J = 2.6 Hz, 2H, Cp), 3.79 (s, 2H, α-CH_2), 1.32 (s, 3H, $C(C\underline{H}_3)_2$), 1.17 (s, 3H, $C(C\underline{H}_3)_2$), 0.24 (s, 18H, $Si(C\underline{H}_3)_3$). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 217.7 (s, Ti-$\underline{C}$=C), 149.2 (s, Ti-C=$\underline{C}$), 137.7 (s, $\underline{C}_6H_{5(ipso)}$), 131.9 (d, J = 162 Hz, Cp), 129.9 (d, J = 162 Hz, Cp), 128.8 (d, J = 161 Hz, Cp), 126.4 (d, J = 160 Hz, $\underline{C}_6H_5$), 124.5 (d, J = 155.5 Hz, $\underline{C}_6H_5$), 124.4 (d, J = 155.5 Hz, $\underline{C}_6H_5$), 124.0 (s, $\underline{C}_6H_{5(ipso)}$), 123.7 (d, J = 172.4 Hz, Cp), 122.2 (s, Cp), 112.5 (d, J = 167.1 Hz, Cp), 111.8 (d, J = 168.7 Hz, Cp), 100.0 (s, Cp), 71.7 (t, J = 137 Hz, α-CH_2), 36.5 (s, $\underline{C}(CH_3)_2$), 23.8 (q, J = 130.8 Hz, $C(\underline{C}H_3)_2$), 23.4 (q, J = 131.4 Hz, $C(\underline{C}H_3)_2$), -0.6 (q, J = 119.2 Hz, $Si(\underline{C}H_3)_3$). IR (cm^{-1}, KBr, cast): 2951 (m), 1593 (m), 1489 (m), 1384 (m), 1368 (m), 1250 (m), 1173 (m), 1152 (m), 1092 (m), 1081 (m), 921 (m), 832 (vs), 769 (m), 756 (s), 737 (s), 714 (m), 697 (s), 689 (s), 632 (m). MS Calcd for $C_{34}H_{42}Si_2Ti$ *m/e* 554.23047, found 554.22830.

Titanacyclobutane 130a from Cinnamyl Complex 107-*meso*:

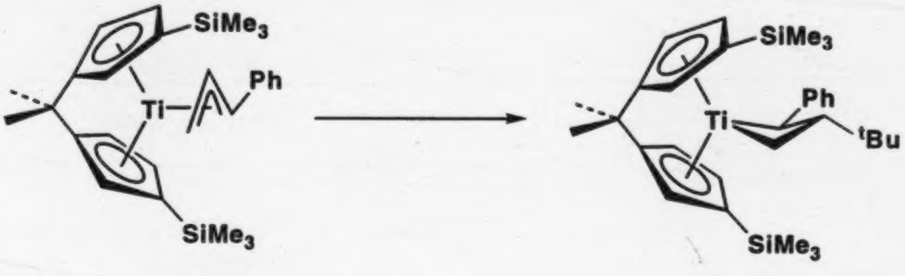


107-*meso*

130a

3-Isopropyl-2-phenyl *meso ansa*-[1]-{dimethylmethano bis(3'-trimethylsilylcyclopentadienyl)}titanacyclobutane 130a. In the drybox, a 25 mL round bottom flask containing a THF solution (5 mL) of *meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium cinnamyl **107-*meso*** (10.0 mg, 0.0209 mmol) and SmI_2 (0.209 mL, 0.1 M in THF) was cooled to -35 °C. 2-Iodopropane (1 equivalent) was added *via* syringe to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was removed *in vacuo* to give a burgundy residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded burgundy micro rods (8.0 mg, 73%). Spectroscopic and high resolution mass spectrometry data for titanacyclobutane **130a**: ^1H NMR (400.1 MHz, C_6D_6): δ 7.25 (t, J = 7.5 Hz, C_6H_5), 7.02 (m, C_6H_5), 6.91 (t, J = 7.1 Hz, C_6H_5), 6.23 (t, J = 2.4 Hz, 1H, Cp), 6.09 (t, *J* = 2.3 Hz, 1H, Cp), 5.45 (t, *J* = 2.4 Hz, 1H, Cp), 5.43 (t, *J* = 2.2 Hz, 1H, Cp), 5.31 (t, *J* = 2.2 Hz, 1H, Cp), 4.19 (t, *J* = 2.5 Hz, 1H, Cp), 4.02 (d, *J* = 12 Hz, 1H, α-$C\underline{H}(C_6H_5)$), 2.61 (t, *J* = 10 Hz, 1H, α-CH_2), 2.48 (t, *J* = 10 Hz, 1H, α-CH_2), 1.55 (m, 1H, $C\underline{H}(CH_3)_2$), 1.29 (s, 3H, $C(C\underline{H}_3)_2$), 1.04 (d, *J* = 6.6 Hz, 3H, $CH(C\underline{H}_3)_2$), 1.03 (s, 3H, $C(C\underline{H}_3)_2$), 0.94 (d, *J* = 6.6 Hz, 3H, $CH(C\underline{H}_3)_2$), 0.85 (m, 1H, β-CH), 0.27 (s, 9H, $Si(C\underline{H}_3)_3$), 0.25 (s, 9H, $Si(C\underline{H}_3)_3$). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 153.9 (s, Ti-CH($C_6H_{5(ipso)}$)), 126.7 (s, Cp), 125.2 (s, Cp), 124.3 (d, *J* = 169.9 Hz, Cp), 121.9 (d, *J* = 158.7 Hz, α-$CH(\underline{C}_6H_5)$), 121.6 (d, *J* = 165.9 Hz, Cp), 119.0 (s, Cp), 118.8 (s, Cp), 114.4 (d, *J* = 171.3 Hz, Cp), 111.9 (d, *J* = 147.7 Hz, α-$CH(\underline{C}_6H_5)$), 111.7 (d, *J* = 167.7 Hz, Cp), 110.6 (d, *J* = 172.9 Hz, Cp), 110.5 (d, *J* = 148.5 Hz, α-$CH(\underline{C}_6H_5)$), 109.5 (d, *J* = 166.9 Hz, Cp), 92.2 (d, *J* = 134.7 Hz, α-$\underline{C}H(C_6H_5)$), 70.0 (t, *J* = 134.3 Hz, α-CH_2), 36.2 (s, $\underline{C}(CH_3)_2$), 34.1 (d, *J* = 123.2 Hz, $\underline{C}H(CH_3)_2$)), 25.0 (q, *J* = 126.7 Hz, $C(\underline{C}H_3)_2$), 23.7 (d, *J* = 152.8 Hz, β-CH), 22.3 (q, *J* = 126.6 Hz, $CH(\underline{C}H_3)_2$), 20.1 (q, *J* = 125.6 Hz, $CH(\underline{C}H_3)_2$), 18.4 (q, *J* = 119.8 Hz, $C(\underline{C}H_3)_2$), -0.32 (q, *J* = 119.2 Hz, $Si(\underline{C}H_3)_3$), -0.73 (q, *J* = 118.4 Hz, $Si(\underline{C}H_3)_3$). IR (cm^{-1}, KBr, cast): 2950 (m), 2899 (m), 2867 (m), 1591 (m), 1487 (m), 1465 (w), 1446 (w), 1402 (w), 1385 (w), 1370 (m), 1247 (s), 1175 (m), 1154 (m), 1127 (w), 1118 (w), 1094 (m), 1080 (m), 1058 (m), 927 (m), 836 (vs), 801 (m), 749 (s), 735 (m), 718 (m), 698 (s), 647 (m), 632 (m), 615 (m). MS Calcd for $C_{31}H_{46}Si_2Ti$ *m/e* 522.26178, found 522.25996. Other important ions include: *m/e* 452.18343 ($C_{26}H_{36}Si_2Ti$, titanocene phenylvinylidene fragment, (0.5); 376.15277 (4%), $C_{20}H_{32}Si_2Ti$); 362.13653 ((100%), $C_{19}H_{30}Si_2Ti$, titanocene template, (100)); 160.12508 ((0.8%), $C_{12}H_{16}$, hydrocarbon fragment of titanacyclobutane), 146.10949 ((7%), $C_{11}H_{14}$, 3-methyl-1-phenylbutene fragment), C_5H_{10}).

Titanacyclobutane 130b from Cinnamyl Complex 107-*meso*:

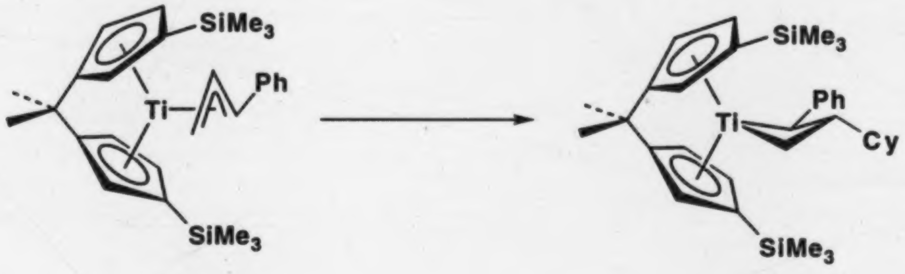


107-*meso* **130b**

3-*tert*-Butyl-2-phenyl *meso ansa*-[1]-{dimethylmethano bis(3'-trimethylsilylcyclopentadienyl)}titanacyclobutane 130b. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of *meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium cinnamyl **107-*meso*** (30.0 mg, 0.0625 mmol) and SmI_2 (0.630 mL, 0.1 M in THF) was cooled to -35 °C. 2-Chloro-2-methylpropane (1 equivalent) was added *via* syringe to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was removed *in vacuo* to give a red-orange residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded burgundy micro rods (30.0 mg, 87%). Spectroscopic and analytical data for titanacyclobutane **130b**: ^1H NMR (400.1 MHz, C_6D_6): δ 7.35 (brs, 2H, α-CH($C_6\underline{H}_5$), 6.90 (brs, 2H, α-CH($C_6\underline{H}_5$), 6.79 (d, *J* = 7.5 Hz, 1H, α-CH($C_6\underline{H}_5$)), 6.57 (brs, 1H, Cp), 6.44 (brs, 1H, Cp), 5.52 (brs, 1H, Cp), 5.41 (brs, 1H, Cp), 5.38 (brs, 1H, Cp), 3.99 (d, *J* = 12 Hz, 1H, α-C$\underline{H}$(C_6H_5)), 3.98 (brs, 1H, Cp), 2.63 (t, *J* = 10 Hz, 1H, α-C$\underline{H}_2$), 2.48 (t, *J* = 10 Hz, 1H, α-C$\underline{H}_2$), 1.28 (s, 3H, C(C$\underline{H}_3$)$_2$), 1.05 (m, 1H, β-CH), 0.96 (s, 9H, C(C$\underline{H}_3$)$_3$), 0.94 (s, 3H, C(C$\underline{H}_3$)$_2$), 0.26 (s, 18H, Si(C$\underline{H}_3$)$_3$). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 154.7 (s, α-CH($\underline{C}_6H_{5(ipso)}$)), 127.3 (s, Cp), 126.4 (s, Cp), 125.8 (d, *J* = 152.9 Hz, α-CH($\underline{C}_6H_5$), 123.9 (d, *J* = 170.5 Hz, Cp), 121.8 (d, *J* = 172.2 Hz, Cp), 121.3

(d, J = 157.5 Hz, α-CH($\underline{C}_6H_5$)), 120.5 (d, J = 146.3 Hz, α-CH($\underline{C}_6H_5$)), 119.9 (s, Cp), 119.8 (s, Cp), 116.4 (d, J = 171.8 Hz, Cp), 112.4 (d, J = 166.9 Hz, Cp), 112.2 (d, J = 175.6 Hz, Cp), 110.4 (d, J = 167.7 Hz, Cp), 85.6 (d, J = 136.1 Hz, α-$\underline{C}$H(C_6H_5)), 69.2 (t, J = 132.8 Hz, α-CH_2), 36.24 (s, $\underline{C}(CH_3)_3$), 36.2 (s, $\underline{C}(CH_3)_2$), 29.6 (q, J = 125.1 Hz, C($\underline{C}H_3)_3$), 25.2 (q, J = 127.4 Hz, C($\underline{C}H_3)_2$), 23.7 (d, J = 127.9 Hz, β-CH), 22.0 (q, J = 122.4 Hz, C($\underline{C}H_3)_2$), -0.13 (q, J = 119.3 Hz, Si($\underline{C}H_3)_3$), -0.66 (q, J = 119.0 Hz, Si($\underline{C}H_3)_3$). IR (cm^{-1}, KBr, cast): 3073 (w), 3013 (w), 2954 (s), 2898 (m), 2871 (m), 1591 (m), 1488 (m), 1370 (m), 1248 (s), 1203 (w), 1175 (m), 1095 (m), 924 (m), 837 (vs), 802 (m), 753 (s), 735 (m), 699 (m), 632 (m). Anal Calcd for $C_{32}H_{48}Si_2Ti$: C, 71.6; H, 9.01. Found C, 71.16; H, 9.24.

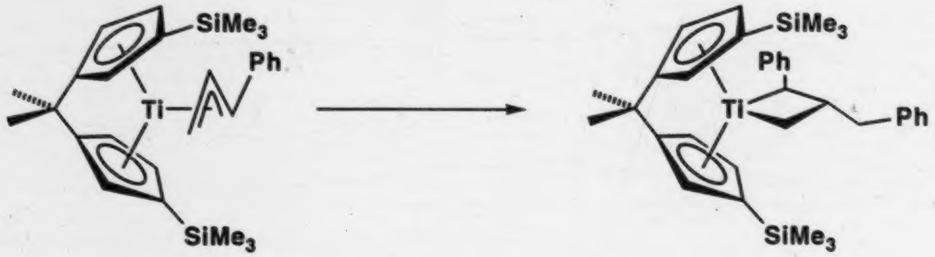
Titanacyclobutane 130c from Cinnamyl Complex 107-*meso*:



107-*meso* **130c**

3-Cyclohexyl-2-phenyl *meso ansa*-[1]-{dimethylmethano bis(3'-trimethylsilylcyclopentadienyl)}titanacyclobutane 130c. In the drybox, a 25 mL round bottom flask containing a THF solution (5 mL) of *meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}titanium cinnamyl **107-*meso*** (10.0 mg, 0.0209 mmol) and SmI_2 (0.209 mL, 0.1 M in THF) was cooled to -35 °C. Cyclohexyl iodide (1 equivalent) was added *via* syringe to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was removed *in vacuo* to give a burgundy residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded burgundy micro rods (11.0 mg, 95%). Spectroscopic and high resolution mass spectrometry data for titanacyclobutane **130c**: ^{1}H NMR (300.1 MHz, C_6D_6): δ 7.25 (t, J = 7.4 Hz, 2H, α-CH($C_6\underline{H}_5$)), 7.00 (brs, 2H, α-CH($C_6\underline{H}_5$)), 6.89 (t, J = 7.2 Hz, 1H, α-CH($C_6\underline{H}_5$)), 6.20 (t, J = 2.4 Hz, 1H, Cp), 6.07 (t, J = 2.2 Hz, 1H, Cp), 5.47 (t, J = 2.4 Hz, 1H, Cp), 5.43 (t, J = 2.1 Hz, 1H, Cp), 5.32 (t, J = 2.1 Hz, 1H, Cp), 4.17 (t, J = 2.4 Hz, 1H, Cp), 4.08 (d, J = 12 Hz, 1H, α-C$\underline{H}$(C_6H_5)), 2.75 (t, J = 10 Hz, 1H, α-C$\underline{H}_2$), 2.55 (t J = 10 Hz, 1H, α-C$\underline{H}_2$), 1.98 (brs, 1H, CH_2(cy)), 1.76 (brs, 4H, CH_2(cy)), 1.60 (brs, 4H, CH_2(cy)), 1.30 (s, 3H, C(C$\underline{H}_3$)$_2$), 1.17 (m, 2H, CH_2(cy)), 1.04 (s, 3H, C(C$\underline{H}_3$)$_2$), 0.85 (m, 1H, β-CH), 0.27 (s, 9H, Si(C$\underline{H}_3$)$_3$), 0.26 (s, 9H, Si(C$\underline{H}_3$)$_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 154.3 (s, α-CH($\underline{C}_6H_{5(ipso)}$)), 126.7 (s, Cp), 125.4 (s, Cp), 124.5 (d, J = 171.9 Hz, Cp), 121.8 (d, J = 158.4 Hz, Cp), 121.5 (d, J = 167.7 Hz, Cp), 119.1 (s, Cp), 118.7 (s, Cp), 114.5 (d, J = 171.6 Hz, Cp), 112.0 (d, J = 148.9 Hz, α-CH($\underline{C}_6H_5$)), 110.5 (d, J = 150.1 Hz, α-CH($\underline{C}_6H_5$)), 109.4 (d, J = 167.4 Hz, Cp), 92.2 (d, J = 132.3 Hz, α-$\underline{C}$H(C_6H_5)), 72.8 (t, J = 137.4 Hz, α-CH_2), 46.2 (d, J = 118.5 Hz, CH(cy)), 36.2 (s, $\underline{C}$(CH_3)$_2$), 32.1 (t, J = 125.7 Hz, CH_2(cy)), 31.9 (t, J = 127.7 Hz, CH_2(cy)), 27.8 (t, J = 130.1 Hz, CH_2(cy)), 27.6 (t, J = 130.1 Hz, CH_2(cy)), 27.4 (t, J = 130.1 Hz, CH_2(cy)), 25.0 (q, J = 126.1 Hz, C($\underline{C}H_3$)$_2$), 22.3 (d, J = 130.4 Hz, β-CH), 17.6 (q, J = 127.3 Hz, C($\underline{C}H_3$)$_2$), -0.3 (q, J = 119.2 Hz, Si($\underline{C}H_3$)$_3$), -0.7 (q, J = 118.6 Hz, Si($\underline{C}H_3$)$_3$). IR (cm^{-1}, KBr, cast): 2950 (m), 2921 (s), 2849 (m), 1592 (m), 1487 (m), 1446 (w), 1370 (w), 1249 (m), 1176 (m), 1154 (w), 1095 (w), 1081 (w), 1059 (w), 928 (m), 835 (vs), 801 (w), 750 (m), 735 (m), 697 (m). MS Calcd $C_{34}H_{50}Si_2Ti$ *m/e* 562.29306. No M$^+$ was observed, however, the fragmentation pattern is similar to the isopropyl and *tert*-butyl analogues, and strongly suggests the presence of this complex. *m/e* (rel intensity): 451.17918 ((2%), $C_{26}H_{35}Si_2Ti$, titanocene phenylvinylidene fragment); 376.15195 ((8%), $C_{20}H_{32}Si_2Ti$, titanocene methylene); 362.13612 ((100), $C_{19}H_{30}Si_2Ti$, titanocene template); 200.15593 ((2%), $C_{15}H_{20}$, hydrocarbon fragment of the titanacyclobutane); 186.14088 ((16%), $C_{14}H_{18}$, 1-cyclohexyl-2-phenylethylene fragment); 110.10944 ((8%), C_8H_{14}, vinylcyclohexyl fragment).

Titanacyclobutane 130d from Cinnamyl Complex 107-*meso*:

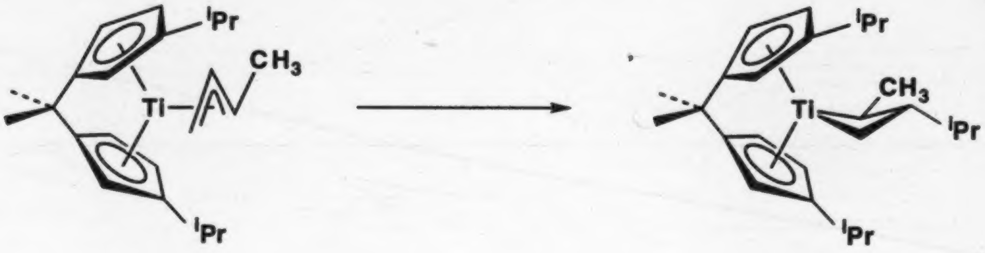


107-*meso* **130d**

3-Benzyl-2-phenyl *meso ansa*-[1]-{dimethylmethano bis(3'-trimethylsilylcyclopentadienyl)}titanacyclobutane 130d. In the drybox, a reaction glass bomb was charged with *meso ansa*-[1]-{dimethylmethano bis(3-trimethylsilylcyclopentadienyl)}-titanium cinnamyl (67.0 mg, 0.1409 mmol), dibenzylmercury (28.0 mg, 0.0705 mmol) and 5 mL of toluene. The sealed vessel was taken out of the drybox and photolyzed with a 450W high pressure mercury lamp at room temperature for 1 h. The glass bomb was taken into the drybox and the solvent was removed *in vacuo* to yield a violet residue, which was triturated with hexane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded violet cubes (75.0 mg, 93%). Spectroscopic and high resolution mass spectrometry data for titanacyclobutane **130d**: ^1H NMR (400.1 MHz, C_6D_6): δ 7.32 (dd, J = 7.0, 6.5 Hz, β-$CH_2(C_6\underline{H}_5)$), 7.26 (d, J = 7.2 Hz, α-$CH_2(C_6\underline{H}_5)$), 7.18 (m, β-$CH_2(C_6\underline{H}_5)$), 7.07 (m, β-$CH_2(C_6\underline{H}_5)$), 6.97 (dd, J

= 8.2, 6.8 Hz, α-$CH_2(C_6\underline{H}_5)$), 6.86 (d, *J* = 7.7 Hz, α-$CH_2(C_6\underline{H}_5)$), 6.20 (brs, 1H, Cp), 6.10 (brs, 1H, Cp), 5.46 (brs, 1H, Cp), 5.37 (brs, 1H, Cp), 5.24 (brs, 1H, Cp), 4.28 (brs, 1H, Cp), 3.95 (d, *J* = 12 Hz, 1H, α-$C\underline{H}(C_6H_5)$), 3.23 (m, 1H, α-CH_2), 2.44 (m, 2H, β-$C\underline{H}_2(C_6H_5)$), 1.91 (t, *J* = 10 Hz, 1H, α-CH_2), 1.26 (s, 3H, $C(C\underline{H}_3)_2$), 1.21 (m, 1H, β-CH), 1.04 (s, 3H, $C(C\underline{H}_3)_2$), 0.28 (s, 9H, $Si(C\underline{H}_3)_3$), 0.04 (s, 9H, $Si(C\underline{H}_3)_3$). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 152.8 (s, α-$CH(\underline{C}_6H_{5(ipso)})$), 142.1 (s, β-$CH_2(C_6H_{5(ipso)})$), 128.7 (d [overlapping of signals prevents determination of coupling constant], β-$CH_2(\underline{C}_6H_5)$), 128.6 (d, β–$CH_2(\underline{C}_6H_5)$), 126.0 (d, β-$CH_2(C_6H_5)$), 125.5 (d, *J* = 179.7 Hz, Cp), 125.3 (s, Cp), 122.3 (d, *J* = 159.7 Hz, α-$CH(\underline{C}_6H_5)$), 121.9 (d, *J* = 160 Hz, α-$CH(\underline{C}_6H_5)$), 118.5 (s, Cp), 118.4 (s, Cp), 113.7 (d, *J* = 170.8 Hz, Cp), 112.1 (d, *J* = 157.9 Hz, α-$CH(\underline{C}_6H_5)$), 110.2 (d, *J* = 177.4 Hz, Cp), 109.6 (d, *J* = 167.7 Hz, Cp), 93.7 (d, *J* = 135.8 Hz, α-$\underline{C}H(C_6H_5)$), 72.6 (t, *J* = 134.4 Hz, α-CH_2), 43.1 (t, *J* = 127.8 Hz, β-$\underline{C}H_2(C_6H_5)$), 36.2 (s, $\underline{C}(CH_3)_2$), 24.8 (q, *J* = 122 Hz, $C(\underline{C}H_3)_2$), 22.4 (q, *J* = 123.4 Hz, $C(\underline{C}H_3)_2$), 16.1 (d, *J* = 131 Hz, β-CH), -0.3 (q, *J* = 119.9 Hz, $Si(\underline{C}H_3)_3$), -1.0 (q, *J* = 120.1 Hz, $Si(\underline{C}H_3)_3$). IR (cm^{-1}, KBr, cast): . MS Calcd $C_{35}H_{46}Si_2Ti$ *m/e* 570.26176. No molecular ion was observed, however, the fragmentation pattern is similar to the isopropyl and *tert*-butyl titanacyclobutanes, and strongly suggests the presence of complex **130d**. *m/e* (rel intensity): 451.17918 ((4%), $C_{26}H_{35}Si_2Ti$, titanocene phenylvinylidene fragment); 362.13715 ((100), $C_{19}H_{30}Si_2Ti$, titanocene template); 208.12382 ((2%), $C_{16}H_{16}$, hydrocarbon fragment of the titanacyclobutane); 194.10866 ((4%), $C_{15}H_{14}$, 1,3-diphenylpropenyl fragment); 118.07678 ((13%), C_9H_{10}, phenylpropenyl fragment).

Titanacyclobutane 131 from Crotyl Complex 110-*meso*:

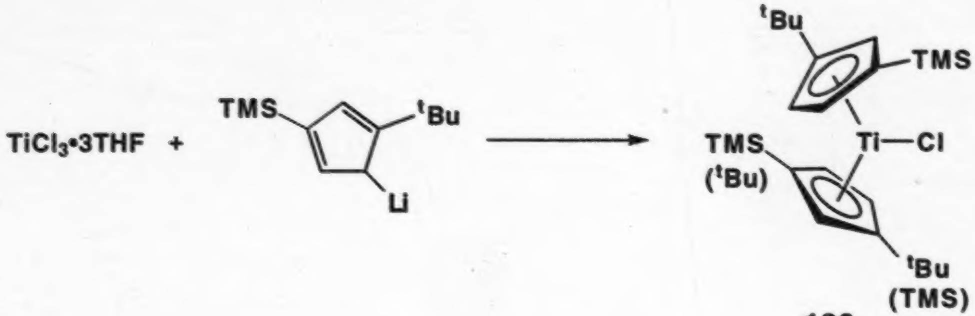


110-*meso* **131**

3-Isopropyl-2-methyl *meso ansa*-[1]-{dimethylsilylbis(3'-isopropylcyclopentadienyl)}titanacyclobutane 131. In the drybox, a 25 mL round bottom flask containing a THF solution (5 mL) of *meso ansa*-[1]-{dimethylmethano bis(3-isopropylcyclopentadienyl)}titanium crotyl **110** (78.0 mg, 0.22 mmol) and SmI$_2$ (0.22 mL, 0.1 M in THF) was cooled to -35 °C. 2-Iodopropane (1 equivalent) was added *via* syringe to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 4 h. The solvent was removed *in vacuo* to give a red-orange residue which was triturated with pentane and the solution filtered through a short column of celite. Concentration of the filtrate and cooling to -35 °C afforded burgundy micro rods (48.0 mg, 55%). Spectroscopic (^{1}H and ^{13}C NMR) data for titanacyclobutane **131**: ^{1}H NMR (300.1 MHz, C$_6$D$_6$): δ 5.60 (brs, 1H, Cp), 5.32 (brs, 1H, Cp), 5.22 (brs, 1H, Cp), 5.13 (brs, 1H, Cp), 5.34 (brs, 1H, Cp), 4.84 (brs, 1H, Cp), 2.75 (dq, *J* = 12.0, 6.0, 1H, α-C$\underline{\text{H}}$(CH$_3$)), 2.60 (m, 1H, C$\underline{\text{H}}$(CH$_3$)$_2$), 2.28 (t, *J* = 10.0, 1H, α-C$\underline{\text{H}}_2$), 1.86 (m, C$\underline{\text{H}}$(CH$_3$)$_2$), 1.80 (t, *J* = 10.0, 1H, α-C$\underline{\text{H}}_2$), 1.80 (m, 1H, C$\underline{\text{H}}$(CH$_3$)$_2$), 1.66 (d, *J* = 6.8, 3H, α-CH(C$\underline{\text{H}}_3$)), 1.34 (s, 3H, C(C$\underline{\text{H}}_3$)$_2$), 1.21 (s, 3H, C(C$\underline{\text{H}}_3$)$_2$), 1.19 (d, *J* = 7.2, 3H, CH(C$\underline{\text{H}}_3$)$_2$), 1.16 (d, *J* = 6.7, 3H, CH(C$\underline{\text{H}}_3$)$_2$), 1.06 (d, *J* = 6.7, 3H, CH(C$\underline{\text{H}}_3$)$_2$), 1.05 (d, *J* = 6.7, 3H, CH(C$\underline{\text{H}}_3$)$_2$), 0.86 (d, *J* = 6.5, 3H, CH(C$\underline{\text{H}}_3$)$_2$), -0.38 (m, 1H, β-CH). ^{13}C{^{1}H} NMR (75.5 MHz, C$_6$D$_6$, APT): δ 138.4 (C$_{\text{(quaternary)}}$), 137.6 (C$_{\text{(quaternary)}}$), 115.1 (C$_{\text{(methine)}}$), 110.4 (C$_{\text{(methine)}}$), 110.1 C$_{\text{(quaternary)}}$), 110.0 C$_{\text{(quaternary)}}$), 106.5

$(C_{(methine)})$, 102.5 $(C_{(methine)})$, 102.3 $(C_{(methine)})$, 99.5 $(C_{(methine)})$, 90.7 $(C_{(methine)})$, 78.3 $(C_{(methylene)})$, 36.2 $(C_{(quaternary)})$, 31.2 $(C_{(methine)})$, 29.0 $(C_{(methine)})$, 28.5 $(C_{(methine)})$, 27.1 $(C_{(methine)})$, 25.6 $(C_{(methyl)})$, 25.2 $(C_{(methyl)})$, 24.7 $(C_{(methine)})$, 24.1 $(C_{(methine)})$, 23.3 $(C_{(methyl)})$, 22.2 $(C_{(methyl)})$, 21.5 $(C_{(methyl)})$, 18.9 $(C_{(methyl)})$.

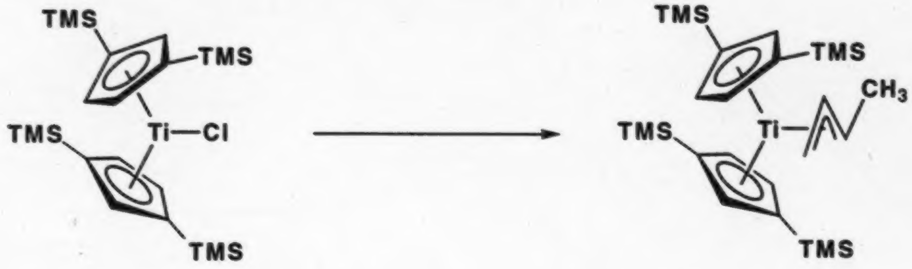
Bis(1-*tert*-butyl-3-trimethylsilylcyclopentadienyl)titanium chloride 136 from $TiCl_3$•3THF and 1-*tert*-butyl-3-trimethylsilylcyclopentadienyllithium:



136

Bis(1-*tert*-butyl-3-trimethylsilylcyclopentadienyl)titanium chloride 136. In a Schlenk flask containing a mixture of 1-*tert*-butyl-3-trimethylsilylcyclopentadienyllithium[221] (2.47 g, 0.0124 mol) and crystalline $TiCl_3$•3THF (2.29 g, 0.0062 mmol) was added 100 mL of THF at room temperature. This reaction mixture was heated at reflux for 10 h under an atmosphere of nitrogen. The solvent was removed to give a dark green residue, which was triturated with pentane and the solution filtered through a sintered-glass funnel layered with celite. Concentration of the pentane filtrate and cooling to -35 °C yielded dark green micro-rods (1.60 g, 55%). Spectroscopic and analytical data for complex **136**: IR (cm^{-1}, KBr, cast): 2959 (s), 2901 (m), 2869 (m), 1460 (m), 1409 (m), 1364 (m), 1248 (s), 1180 (m), 1091 (m), 1075 (m), 1064 (m), 1055 (m), 1022 (m), 940 (m), 919 (m), 860 (s), 837 (vs), 754 (s), 694 (m), 678 (m), 665 (m), 635 (m), 624 (m). Anal Calcd for $C_{24}H_{42}Si_2Ti$: C, 61.32; H, 9.01. Found C, 61.08; H, 9.10.

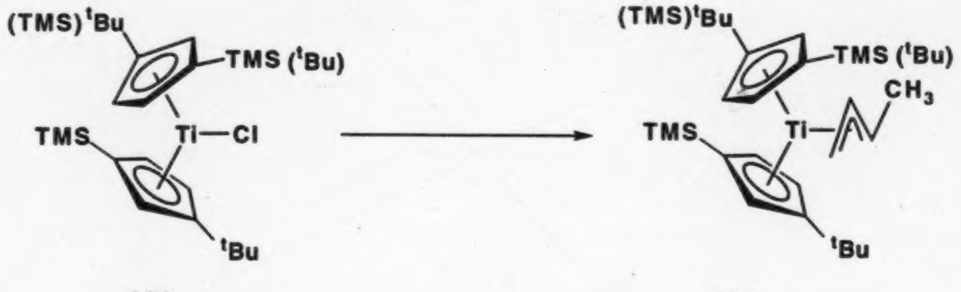
Crotyl Complex 137 from Titanocene Chloride 135:



135 137

Bis(1,3-bis(trimethylsilyl)cyclopentadienyl)titanium crotyl 137. In the drybox, a 25-mL round bottom flask containing bis(1,3-bis(trimethylsilyl)cyclopentadienyl)titanium chloride[134,222] **135** (161 mg, 0.361 mmol) in 5 mL of THF was cooled to -35 °C. Crotylmagnesium chloride (241 μL, 1.5 M in THF) was then added to this cooled solution. After 10 minutes at -35 °C, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Removal of the solvent *in vacuo* yielded a dark purple residue which was triturated with pentane. Evaporation of the pentane gave a violet oil (168 mg, 89%) which failed to yield any crystalline material on cooling to -35 °C. Spectroscopic (infrared only) data for complex **137**: IR (cm^{-1}, KBr, cast): 3088 (m), 2953 (vs), 2897 (s), 2854 (m), 1543 (w, η^3-allyl), 1514 (w), 1446 (s), 1403 (m), 1374 (m), 1325 (m), 1247 (vs), 1206 (s), 1086 (vs), 1024 (m), 960 (m), 920 (vs), 830 (vs), 754 (vs), 690 (s), 637 (s), 484 (m).

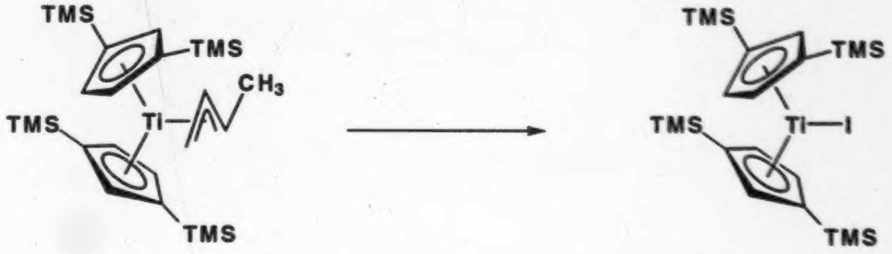
Crotyl Complex 138 from Titanocene Chloride 136:



136 **138**

Bis(1-*tert*-butyl-3-trimethylsilylcyclopentadienyl)titanium crotyl 138. In the drybox, a 25-mL round bottom flask containing bis(1-*tert*-butyl-3-trimethylsilylcyclopentadienyl)titanium chloride **136** (107 mg, 0.227 mmol) in 5 mL of THF was cooled to -35 °C. Crotylmagnesium chloride (152 µL, 1.5 M in THF) was then added to this cooled solution. After 10 minutes at - 35 °C, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Removal of the solvent *in vacuo* yielded a dark purple residue which was triturated with pentane. Evaporation of the pentane gave a violet oil (108 mg, 97%) which failed to yield any crystalline material on cooling to -35 °C. This material was investigated for radical alkylation reactivity without further characterization.

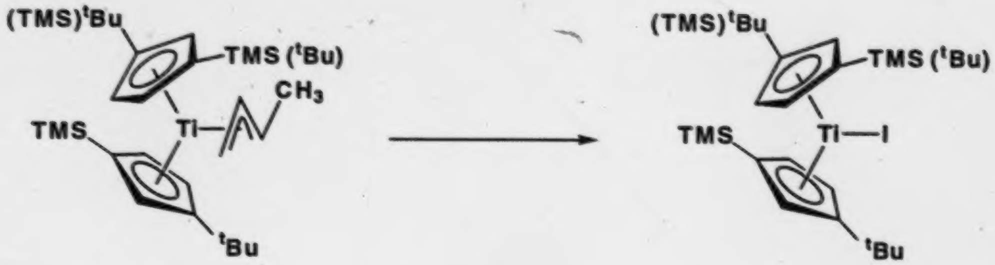
Titanocene Iodide 139 from Crotyl Complex 137:



137 **139**

Bis(1,3-bis(trimethylsilyl)cyclopentadienyl)titanium iodide 139. In the drybox, a 25-mL round bottom flask containing a THF solution (5 mL) of bis(1,3-bis(trimethylsilyl)cyclopentadienyl)titanium crotyl **137** (168 mg, 0.32 mmol) and SmI$_2$ (3.2 mL, 0.1 M in THF) was cooled to -35 °C. 2-Iodopropane (1 equivalent) was added to this cooled solution and after 10 minutes at -35 °C, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was removed *in vacuo* to yield a dark blue-green residue which was triturated with pentane and the solution filtered through a sintered-glass funnel layered with celite. The filtrate was concentrated and cooled to -35 °C to yield blue-green needles (115 mg, 60%). Spectroscopic and analytical data for complex **139**: IR (cm^{-1}, KBr, cast): 2853 (m), 2897 (m), 1766 (w), 1445 (m), 1402 (m), 1391 (m), 1322 (w), 1262 (m), 1242 (vs), 1203 (m), 1092 (s), 924 (s), 919 9s), 884 (s), 828 (vs), 72 (s), 687 (m), 665 (w), 634 (m), 616 (m), 479 (m). Anal Calcd for C$_{22}$H$_{42}$Si$_4$TiI: C, 44.51; H, 7.13. Found C, 44.9; H, 7.28.

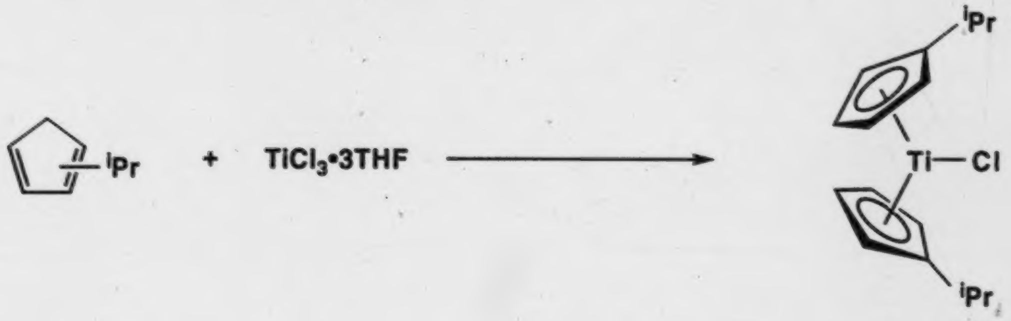
Titanocene Iodide 140 from Crotyl Complex 138:



138 **140**

Bis(1-*tert*-butyl-3-trimethylsilylcyclopentadienyl)titanium iodide 140. In the drybox, a 25-mL round bottom flask containing a THF solution (5 mL) of bis(1-*tert*-butyl-3-trimethylsilylcyclopentadienyl)titanium crotyl **138** (108 mg, 0.22 mmol) and SmI$_2$ (2.2 mL, 0.1 M in THF) was cooled to -35 °C. 2-Iodopropane (1 equivalent) was added to this cooled solution and after 10 minutes at -35 °C, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was removed *in vacuo* to yield a dark blue-green residue which was triturated with pentane and the solution filtered through a sintered-glass funnel layered with celite. The filtrate was concentrated and cooled to -35 °C to yield blue-green needles (74.0 mg, 60%). Spectroscopic and high resolution mass spectrometry data for complex **140**: IR (cm^{-1}, KBr, cast): 2958 (m), 2900 (w), 2863 (w), 1459 (w), 1363 (w), 1247 (s), 1178 (w), 1090 (w), 1059 (w), 915 (w), 869 (m), 860 (m), 837 (vs), 754 (s), 693 (w), 636 (w). MS Calcd for C$_{24}$H$_{42}$Si$_2$TiI *m/e* 561.13495, found 561.13491.

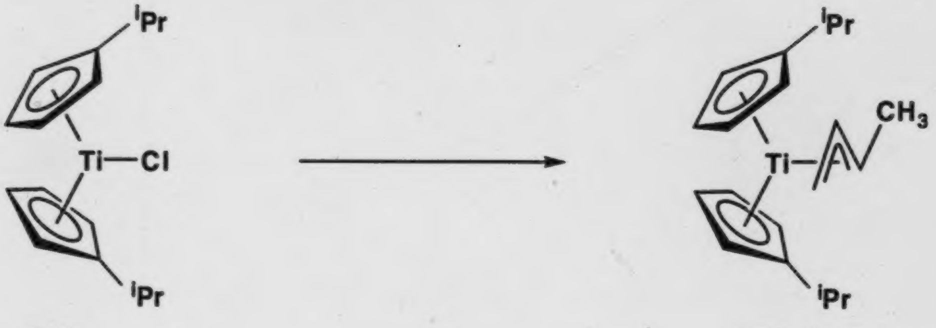
Titanocene Chloride 141 from Lithium salt of Isopropylcyclopentadienyl:



141

Bis(isopropylcyclopentadienyl)titanium chloride 141. The lithium salt of isopropylcyclopentadiene (1.80 g, 15.8 mmol) and $TiCl_3$•3THF (2.92 g, 7.89 mmol) were mixed together in a 100 mL Schlenk flask fitted with a rubber septum and cooled to - 78 °C. THF (50 mL) cooled to -78 °C was transferred by cannula from a second 100 mL Schlenk flask onto the solids. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. The solvent was removed *in vacuo* and the resulting green residue was triturated with pentane and the solution filtered through a sintered-glass funnel layered with celite. The filtrate was concentrated and cooled to -35 °C to yield complex **141** (1.20 g, 50%). Characterization of this complex was done indirectly by $PbCl_2$ oxidation (0.5 equivalent $PbCl_2$ in THF at room temperature for 1 h) to yield the known bis(isopropylcyclopentadienyl) dichloride.[135]

Crotyl Complex 142 from Titanocene Chloride 141:

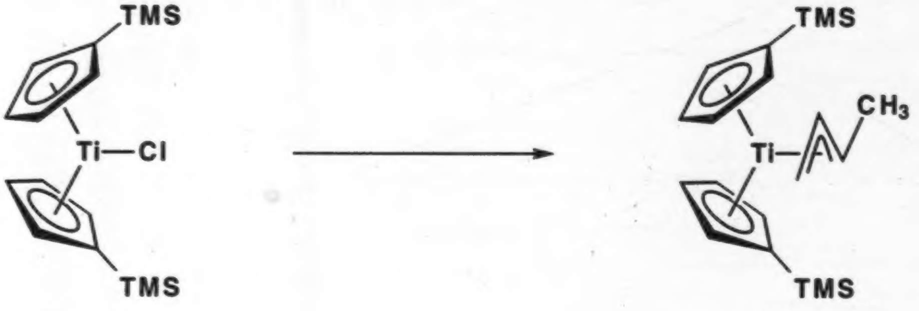


141

142

Bis(isopropylcyclopentadienyl)titanium crotyl 142. In the drybox, a 50 mL round bottom flask containing a THF solution (20 mL) of bis(isopropylcyclopentadienyl)titanium chloride **141** (219 mg, 0.735 mmol) was cooled to -35 °C. Crotylmagnesium chloride (490 µL, 1.5 M in THF) was added to the cooled solution and after 10 minutes at -35 °C, the reaction mixture was allowed to warm to room temperature and subsequently stirred for 1 h. Removal of the solvent *in vacuo* yielded a dark purple residue which was triturated with pentane and the solution filtered through a sintered-glass funnel layered with celite. Concentration of the filtrate and cooling to -35 °C yielded dark purple cubes (50.0 mg, 21%). This air-sensitive paramagnetic crotyl complex was characterized by infrared spectroscopy and elemental analysis: IR (cm^{-1}, KBr, cast): 2959 (vs), 2923 (vs), 2892 (s), 2890 (vs), 2852 (s), 1539 (m, η^3-allyl),[115,213] 1490 (m), 1456 (s), 1417 (m), 1379 (m), 1360 (m), 1315 (m), 1200 (w), 1150 (w), 1104 (w), 1079 (m), 1061 (m), 1033 (s), 1005 (m), 931 (m), 956 (s), 791 (vs), 746 s. Anal Calcd for $C_{20}H_{29}Ti$: C 75.70, H, 9.21. Found C, 75.25; H, 9.28.

Crotyl Complex 144 from Titanocene Chloride 143:



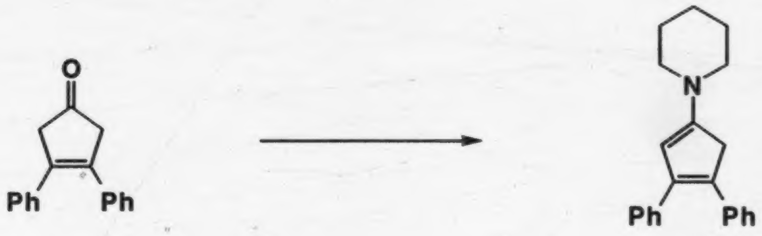
143

144

Bis(trimethylsilylcyclopentadienyl)titanium crotyl 144. In the drybox, a 50 mL round bottom flask containing a THF solution (20 mL) of bis(trimethylsilylcyclopentadienyl)titanium chloride[136] **143** (75.0 mg, 0.209 mmol) was cooled to -35 °C. Crotylmagnesium chloride (140 µL, 1.5 M in THF) was added to the cooled solution and after 10 minutes at -35 °C, the reaction mixture was allowed to warm to room temperature and subsequently stirred for 1 h. Removal of the solvent yielded a dark purple residue which was triturated with pentane and the solution filtered through a sintered-glass funnel layered with celite. Concentration of the filtrate and cooling to -35 °C yielded dark purple cubes (55.0 mg, 50%). This air-sensitive paramagnetic crotyl complex was characterized by infrared spectroscopy and high resolution mass spectrometry: IR (cm^{-1}, KBr, cast): 2954 (m), 2896 (w), 2850 (m), 1550 (w), 1246 (s), 1176 (m), 1051 (m), 832 (vs), 803 (vs), 752 (s), 688 (m). MS Calcd for $C_{20}H_{33}Si_2Ti$ *m/e* 377.16003, found 377.16079.

2.3.4 Radical Addition to DialkylaminocyclpentadienylTitanium(III) η^3-Allyl Complexes

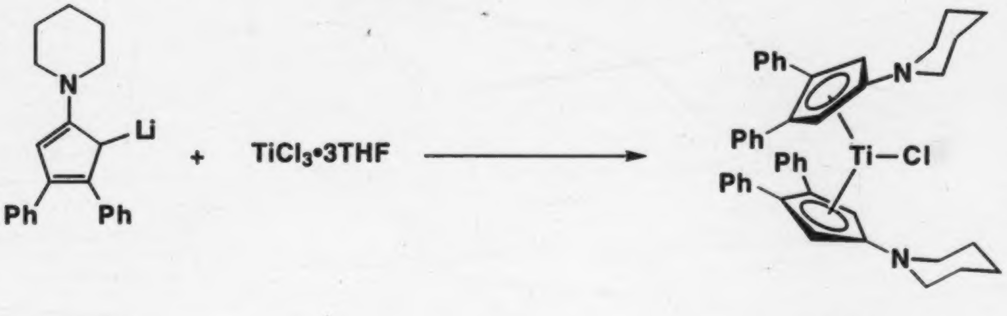
Enamine 145 from 3,4-Diphenylcyclopentenone:



145

1-Piperidino-3,4-diphenylcyclopentadiene 145. 3,4-diphenylcyclopent-2-enone[68,137] (10.0 g, 42.7 mmol), piperidine (5.0 mL, mmol) and *p*-toluenesulfonic acid (0.05 mg) in benzene (100 mL) were heated under reflux for 48 h with a water aspirator attached to the reflux apparatus. After the removal of solvent *in vacuo* the residue was recrystallized from diethyl ether four times to yield a yellow-brown powder (9.23 g, 72%). Spectroscopic (^{1}H NMR only) and high resolution mass spectrometry data for compound **145**: ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.31 (m, 10H, C_6H_5), 5.33 (s, 1H), 3.49 (s, 2H), 3.11 (t, J = 5.5 Hz, 4H), 1.67 (m, 4H), 1.59 (m, 2H). MS Calcd for $C_{22}H_{23}N$ *m/e* 301.18304, found 301.18397.

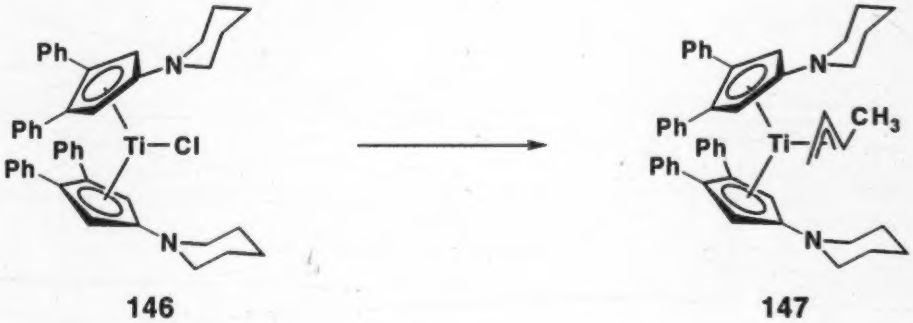
Titanocene Chloride 146 from Lithium salt of Enamine 145:



145-Li$_2$ **146**

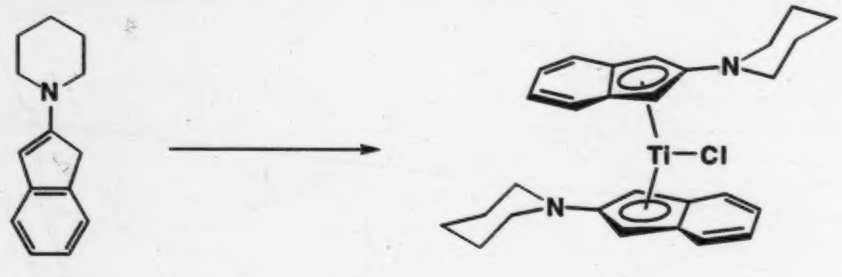
Bis(3,4-diphenyl-1-piperidinocyclopentadienyl)titanium chloride 146. In the drybox, the lithium salt of 3,4-diphenyl-1-piperidinocyclopentadiene **145** (8.06 g, 26.2 mmol) and $TiCl_3$•3THF (4.86 g, 13.1 mmol) were placed in a 500 mL 3-necked round bottom flask fitted with a gas-adapter, glass stopper and rubber septum. To a second flask (Schlenk flask) was placed 200 mL of THF. The contents of both flasks were cooled to -78 °C for 0.5 h and then the THF was transferred *via* cannula onto the mixed solids. After 2 h at this temperature, the reaction mixture was allowed to warm to room temperature and stirred for 4 h. The solvent was removed *in vacuo* leaving a dark brown residue. Trituration of the residue with benzene and filtration of the solution through a sintered glass funnel layered with celite gave a dark brown filtrate. The benzene was removed *in vacuo* and the resulting residue was crystallized from a THF/hexane solution (1 : 6) yielding a dark brown amorphous solid (2.23 g, 36%). Spectroscopic (infrared only) data for complex **146**: IR (cm^{-1}, KBr, diethyl ether cast): 3057 (m), 2933 (vs), 2855 (s), 2808 (m), 1600 (s), 1577 (m), 1527 (s), 1500 (vs), 1450 (vs), 1386 (s), 1357 (m), 1258 (m), 1216 (m), 1155 (m), 1119 (s), 1073 (s), 1026 (m), 764 (vs), 698 (vs). Further support for monochloride complex **146** is garnered from $PbCl_2$ oxidation (0.5 equivalent $PbCl_2$ in THF at room temperature for 1 h) to give the corresponding diamagnetic dichloride complex. Spectroscopic (^{1}H NMR only) data: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.38 (2nd order multiplet, 8H, C_6H_5), 7.22 (2nd order multiplet, 12H, C_6H_5), 5.71 (s, 4H, Cp), 3.14 (brs, 8H, piperidino), 1.55 (brs, 12H, piperidino).

Titanocene Crotyl 147 from Titanocene Chloride 146:



Bis(3,4-diphenyl-1-piperidinocyclopentadienyl)titanium crotyl 147. In the drybox, a 25 mL round bottom flask containing a THF solution (15 mL) of 3,4-diphenyl-1-piperidinocyclopentadienyl)titanium chloride **146** (777 mg, 1.14 mmol) was cooled to -35 °C. Crotylmagnesium chloride (0.760 mL, 1.5 M in THF) was added to the cooled solution and after 45 minutes at this temperature, the reaction mixture was allowed to warm to room temperature and stirred for a further 2 h. The solvent was removed *in vacuo* giving a dark brown residue, which was triturated with benzene and the solution filtered through a sintered-glass funnel layered with celite. Evaporation of the benzene gave a dark brown residue which was crystallized from toluene cooled to -35 °C to give a dark brown amorphous solid (384 mg, 48%). Spectroscopic (infrared only) data for complex **147**: IR (cm^{-1}, KBr, diethyl ether cast): 2933 (m), 2856 (m), 1598 (m), 1543 (w), 1524 (w), 1499 (m), 1467 (w), 1459 (w), 1450 (m), 1384 (w), 1117 (m), 1070 (w), 763 (m), 698 (vs).

Titanocene Chloride 149 from Lithium salt of Enamine 148:

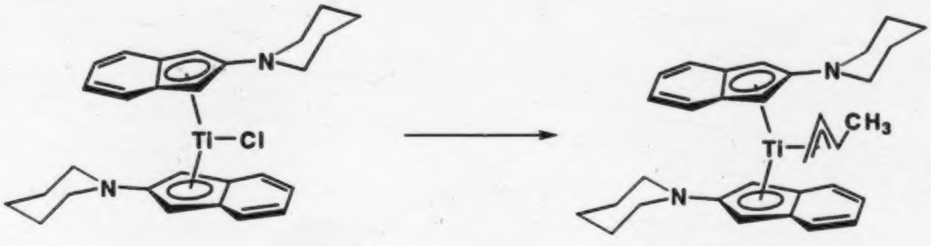


148 **149**

Bis(2'-piperidinoindenyl)titanium chloride 149. In the drybox, the lithium salt of 2-piperidinoindene[138,139] **148** (3.62 g, 17.6 mmol) and $TiCl_3$•3THF (3.27 g, 8.82 mmol) were placed in a 3-necked round bottom flask fitted with a gas adapter, glass stopper and rubber septum. To a second flask (Schlenk) was placed 75 mL of THF. The contents of both flasks were cooled to -78 °C for 1 h and the THF was transferred *via* cannula onto the solids. After 2 h at this temperature, the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The solvent was removed *in vacuo* yielding a greenish-brown residue which was triturated with benzene and the solution filtered through a sintered glass funnel layered with celite. The benzene was removed *in vacuo* and the resulting residue was crystallized from a THF/hexane (1 : 6) solution, yielding monochloride complex as a pale yellow-green paramagnetic amorphous solid (2.66g, 70%). Oxidation of a sample of monochloride complex **149** with 0.5 equivalent $PbCl_2$ in THF at room temperature for 1 h gave the corresponding diamagnetic dichloride complex. Spectroscopic (^{1}H NMR and ^{13}C only) data for the dichloride complex: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.78 (2nd order multiplet, 4H, indenyl), 7.24 (2nd order multiplet, 4H, indenyl), 4.12 (s, 4H, indenyl), 3.12 (brs, 8H, piperidino), 1.67 (brs, 6H, piperidino), 1.38 (brs, 6H, piperidino). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, APT): δ

160.6 ($C_{quaternary}$), 127.0 ($C_{methine}$), 125.6 ($C_{quaternary}$), 123.8 ($C_{methine}$), 91.9 ($C_{methine}$), 46.6 ($C_{methylene}$), 25.4 ($C_{methylene}$), 23.4 ($C_{methylene}$).

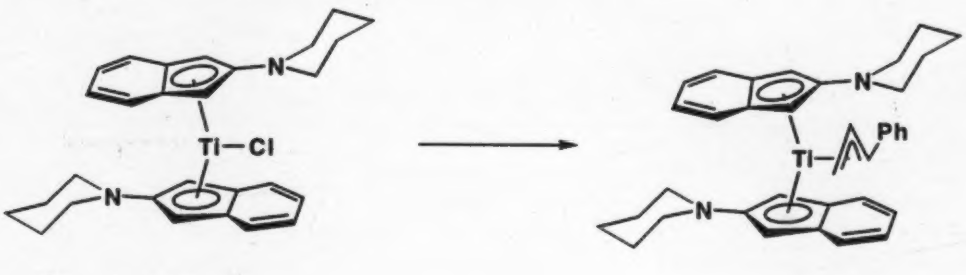
Titanocene Crotyl 150 from Titanocene Chloride 149:



149 **150**

Bis(2'-piperidinoindenyl)titanium crotyl 150. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of bis(2'-piperidinoindenyl)titanium chloride **149** (0.456 g, 0.950 mmol) was cooled to -35 °C. Crotylmagnesium chloride (0.633 mL, 1.5 M in THF) was added to the cooled solution and after 45 minutes at this temperature, the reaction mixture was allowed to warm to room temperature and stirred for a further 2 h. The THF was removed *in vacuo* giving a dark brown residue, which was triturated with benzene and the solution filtered through a sintered-glass funnel layered with celite. Evaporation of the benzene gave a dark brown residue which was crystallized from cold (– 35 °C) toluene to give a dark brown amorphous solid (240 mg, 51%). Spectroscopic (infrared only) data for complex **150**: IR (cm^{-1}, KBr, cast): 2933 (vs), 2852 (m), 1583 (s), 1568 (s), 1541 (s), 1513 (s), 1505 (s), 1462 (s), 1448 (vs), 1385 (m), 1361 (m), 1313 (m), 1258 (m), 1195 (m), 1125 (s), 1025 (m), 792 (m), 739 (m), 679 (m), 668 (m), 455 (m).

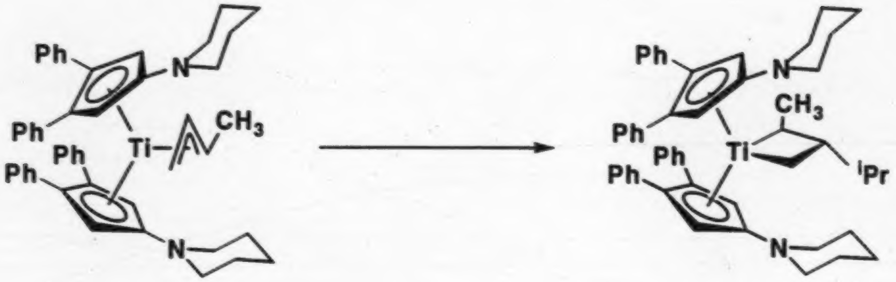
Titanocene Cinnamyl 151 from Titanocene Chloride 149:



149 **151**

Bis(2'-piperidinoindenyl)titanium cinnamyl 151. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of bis(2'-piperidinoindenyl)titanium chloride **149** (1.73 g, 3.61 mmol) was cooled to -35 °C. A cooled THF solution of cinnamyllithium (0.44 g in 2 mL THF) was added to the monochloride solution and after 45 minutes at this temperature, the reaction mixture was allowed to warm to room temperature and stirred for a further 2 h. The THF was removed *in vacuo* giving a dark green residue, which was triturated with benzene and the solution filtered through a sintered-glass funnel layered with celite. Evaporation of the benzene gave a dark green residue. Crystallization from cold (-35 °C) diethyl ether gave dark green cubes (1.03 g, 51%). Spectroscopic (infrared only) and analytical data for complex **151**: IR (cm^{-1}, KBr, cast): 2933 (vs), 2852 (m), 2806 (m), 1592 (m), 1569 (m), 1538 (m), 1530 (m), 1494 (s), 1449 (vs), 1385 (m), 1362 (m), 1125 (m), 802 (m), 739 (s). Anal. Calcd for $C_{37}H_{41}TiN_2$: C, 79.13; H, 7.36; N, 4.99. Found C, 78.79; H, 7.51; N, 4.94. Selected X-ray crystallographic data for complex **151** are listed at the end of experimental section (p. 263).

Titanacyclobutane 152a from Crotyl Complex 147:

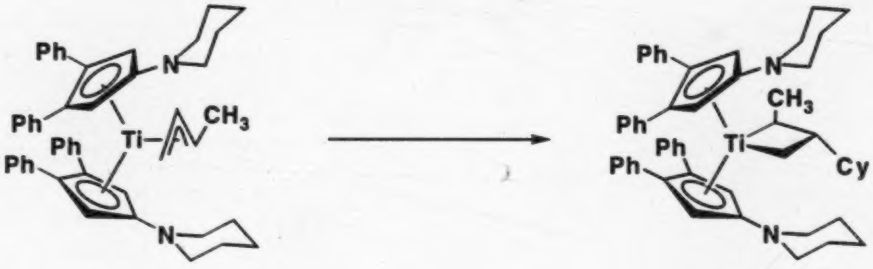


147 **152a**

3-Isopropyl-2-methyl bis(3',4'-diphenyl-1'-piperidinocyclopentadienyl)titanacyclobutane 152a. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of 3,4-diphenyl-1-piperidinocyclopentadienyl)titanium crotyl **147** (27.0 mg, 0.0384 mmol) and SmI_2 (384 µL, 0.1 M in THF) was cooled to -35 °C. 2-Iodopropane (1 equivalent) was added to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 20 minutes. The solvent was removed *in vacuo* and the resulting red-brown residue was triturated with benzene and the solution filtered through a sintered-glass funnel layered with celite. Evaporation of the benzene, followed by crystallization in cold (-35 °C) diethyl ether yielded dark red-brown needles (16.0 mg, 56%). As a result of the thermal instability of titanacyclobutane **152a** only the ^{1}H NMR data is reported: ^{1}H NMR (400.1 MHz, C_6D_6): δ 7.61 (t, J = 6.9 Hz, 4H, $C_6\underline{H}_5$), 7.52 (d, J = 7.7 Hz, 2H, $C_6\underline{H}_5$), 7.43 (d, J = 7.1 Hz, 2H, $C_6\underline{H}_5$), 7.26 (t, J = 7.7 Hz, 2H, $C_6\underline{H}_5$), 7.11 (m, 4H, $C_6\underline{H}_5$), 7.03 (m, 5H, $C_6\underline{H}_5$), 6.89 (t, J = 7.1 Hz, 1H, $C_6\underline{H}_5$), 6.01 (d, J = 2.8 Hz, 1H, Cp), 5.53 (d, J = 3.0 Hz, 1H, Cp), 5.36 (d, J = 2.8 Hz, 1H, Cp), 4.58 (d, J = 2.7 Hz, 1H, Cp), 2.81 (m, 4H, $CH_{2(piperidino)}$), 2.70 (t, J = 10.0 Hz, 1H, α-CH_2), 2.61 (m, 3H, $CH_{2(piperidino)}$, α-$C\underline{H}(CH_3)$), 2.39 (m, 2H, $CH_{2(piperidino)}$), 2.39 (t, J = 10.0 Hz, 1H, α-CH_2), 1.67 (d, J = 6.8 Hz, 3H, α-$CH(CH_3)$, 1.43 (m, 6H, $CH_{2(piperidino)}$), 1.27 (m, 3H,

$CH_{2(piperidino)}$), 1.23 (m, 3H, $CH_{2(piperidino)}$), 1.06 (d, *J* = 6.6 Hz, 3H, $CH(C\underline{H}_3)_2$), 1.00 (d, *J* = 6.6 Hz, 3H, $CH(C\underline{H}_3)_2$), -0.10 (m, 1H, β-CH).

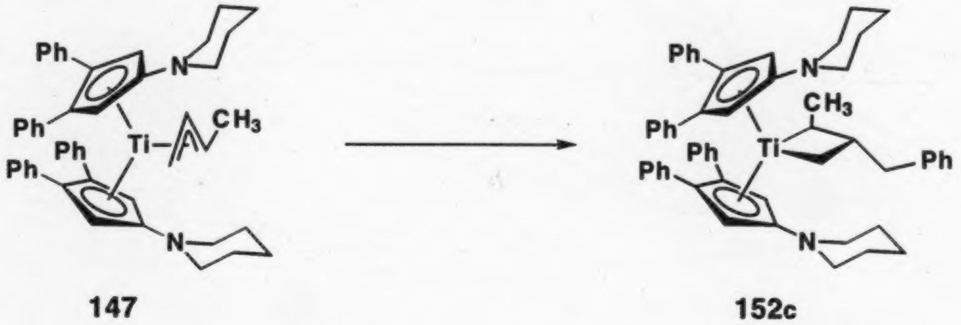
Titanacyclobutane 152b from Crotyl Complex 147:



147 **152b**

3-Cyclohexyl-2-methyl bis(3',4'-diphenyl-1'-piperidinocyclopentadienyl) titana cyclobutane 152b. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of 3,4-diphenyl-1-piperidinocyclopentadienyl)titanium crotyl **147** (24.0 mg, 0.0341 mmol) and SmI_2 (341 μL, 0.1 M in THF) was cooled to -35 °C. Cyclohexyl iodide (1 equivalent) was added to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 20 minutes. The solvent was removed *in vacuo* and the resulting red-brown residue was triturated with benzene and the solution filtered through a sintered-glass funnel layered with celite (1 inch). Evaporation of the benzene, followed by crystallization in cold (-35 °C) diethyl ether yielded dark red-brown needles (18.0 mg, 67%). As a result of the thermal instability of titanacyclobutane **152b** only the ^1H NMR data is reported: ^1H NMR (400.1 MHz, C_6D_6): δ 7.61 (m, 4H, $C_6\underline{H}_5$), 7.50 (d, *J* = 7.7 Hz, 2H, $C_6\underline{H}_5$), 7.44 (d, *J* = 7.3 Hz, 2H, $C_6\underline{H}_5$), 7.22 (dd, *J* = 7.7, 7.3 Hz, 2H, $C_6\underline{H}_5$), 7.12 (m, 4H, $C_6\underline{H}_5$), 7.04 (m, 5H, $C_6\underline{H}_5$), 6.92 (dd, *J* = 7.4, 7.3 Hz, 1H, $C_6\underline{H}_5$), 6.04 (d, *J* = 2.8 Hz, 1H, Cp), 5.59 (d, *J* = 3.0 Hz, 1H, Cp), 5.34 (d, $J = 2.9$ Hz, 1H, Cp), 4.66 (d, $J = 2.9$ Hz, 1H, Cp), 2.86 (t, $J = 10.0$ Hz, 1H, α-CH_2), 2.72 (m, 2H, α-C$\underline{H}$(CH_3), $CH_{2((cy))}$), 2.68 (m, 2H, $CH_{2(piperidino)}$), 2.49 (m, 2H, $CH_{2(piperidino)}$), 2.38 (t, $J = 10.0$ Hz, 1H, α-CH_2), 1.96 (m, 1H, $CH_{2((cy))}$), 1.81 (m, 5H, $CH_{2((cy))}$), 1.74 (d, $J = 6.8$ Hz, 3H, α-CH(C$\underline{H}_3$)), 1.63 (m, 2H, $CH_{2((cy))}$), 1.45 (m, 6H, $CH_{2(piperidino)}$), 1.28 (m, 3H, $CH_{2(piperidino)}$), 1.23 (m, 3H, $CH_{2(piperidino)}$), 1.05 (m, 2H, $CH_{2((cy))}$), -0.24 (m, 1H, β-CH).

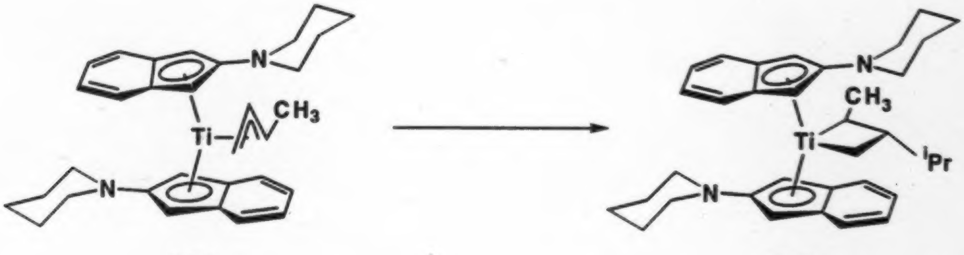
Titanacyclobutane 152c from Crotyl Complex 147:



3-Benzyl-2-methyl bis(3',4'-diphenyl-1'-piperidinocyclopentadienyl)titanacyclobutane 152c. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of 3,4-diphenyl-1-piperidinocyclopentadienyl)titanium crotyl (21.0 mg, 0.0298 mmol) and SmI_2 (298 µL, 0.1 M in THF) was cooled to -35 °C. Benzyl chloride (1 equivalent) was added to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 20 minutes. The solvent was removed *in vacuo* and the resulting red-brown residue was triturated with benzene and the solution filtered through a sintered-glass funnel layered with celite. Evaporation of the benzene followed by crystallization in cold (-35 °C) diethyl ether yielded dark red-brown needles (5.0 mg, 20%). As a result of the thermal instability of titanacyclobutane **152c** only the ^{1}H NMR

data are reported: ^{1}H NMR (400.1 MHz, C_6D_6): δ 7.77 (m, $C_6\underline{H}_5$), 7.66 (m, $C_6\underline{H}_5$), 7.53 (m, $C_6\underline{H}_5$), 7.46 (m, $C_6\underline{H}_5$), 7.34 (m, $C_6\underline{H}_5$), 7.02 (m, $C_6\underline{H}_5$), 6.33 (d, J = 3.1 Hz, 1H, Cp), 6.07 (d, J = 3.2 Hz, 1H, Cp), 5.58 (d, J = 2.9 Hz, 1H, Cp), 5.29 (d, J = 2.9 Hz, 1H, Cp), 2.93 (m, 4H, $CH_{2(piperidino)}$), 2.60 (m, 2H, $CH_{2((piperidino))}$), 2.47 (t, J = 10.0 Hz, 1H, α-CH_2), 2.39 (m, 3H, α-$C\underline{H}(CH_3)$, $C\underline{H}_2C_6H_5$), 2.27 (t, J = 10 Hz, 1H, α-CH_2), 1.78 (d, J = 6.8 Hz, 3H, α-$CH(C\underline{H}_3)$), 1.45 (m, 6H, $CH_{2(piperidino)}$), 1.23 (m, 3H, $CH_{2(piperidino)}$), 1.15 (m, 3H, $CH_{2(piperidino)}$), 0.01 (m, 1H, β-CH).

Titanacyclobutane 153a from Crotyl Complex 150:

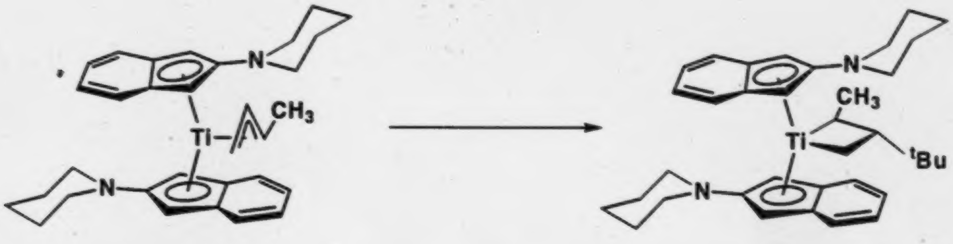


150 **153a**

3-Isopropyl-2-methyl bis(2'-piperidinoindenyl)titanacyclobutane 153a. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of bis(2'-piperidinoindenyl)titanium crotyl **150** (100 mg, 0.20 mmol) and SmI_2 (2.0 mL, 0.1 M in THF) was cooled to -35 °C. 2-Iodopropane (1 equivalent) was added to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 45 minutes. The solvent was removed *in vacuo* and the resulting red-brown residue was triturated with benzene and the solution filtered through a sintered-glass funnel layered with celite. Removal of benzene followed by crystallization in cold (-35 °C) diethyl ether yielded dark red-brown needles (75.0 mg, 69%). As a result of the thermal instability of titanacyclobutane **153a** only the ^{1}H NMR data is reported: ^{1}H NMR (300.1

MHz, C_6D_6): δ 7.43 (d, *J* = 7.7 Hz, 1H, In), 7.30 (dd, *J* = 7.6, 6.8 Hz, 1H, In), 7.15 (m, 2H, In), 7.01 (dd, *J* = 7.9, 7.2 Hz, 1H, In), 6.93 (m, 2H, In), 6.85 (dd, *J* = 7.7, 7.0 Hz, 1H, In), 5.42 (d, *J* = 2.0 Hz, 1H, In), 5.24 (d, *J* = 2.1 Hz, 1H, In), 4.80 (brs, 1H, In), 4.66 (brs, 1H, In), 2.84 (m, 4H, $CH_{2(piperidino)}$), 2.70 (m, 4H, $CH_{2(piperidino)}$), 2.53 (t, *J* = 10.0 Hz, 1H, α-CH_2), 1.96 (m, 1H, $C\underline{H}(CH_3)_2$), 1.86 (d, *J* = 6.4 Hz, 3H, α-$CH(C\underline{H}_3)$), 1.70 (dq, *J* = 12.0, 6.4 Hz, 1H, α-$C\underline{H}(CH_3)$), 1.37 (m, 6H, $CH_{2(piperidino)}$), 1.26 (m, 1H, $CH_{2(piperidino)}$), 1.18 (d, *J* = 6.6 Hz, 3H, $CH(C\underline{H}_3)_2$), 1.08 (d, *J* = 6.6 Hz, 3H, $CH(C\underline{H}_3)_2$), 0.33 (t, *J* = 10.0 Hz, 1H, α-CH_2), -0.24 (m, 1H, β-CH).

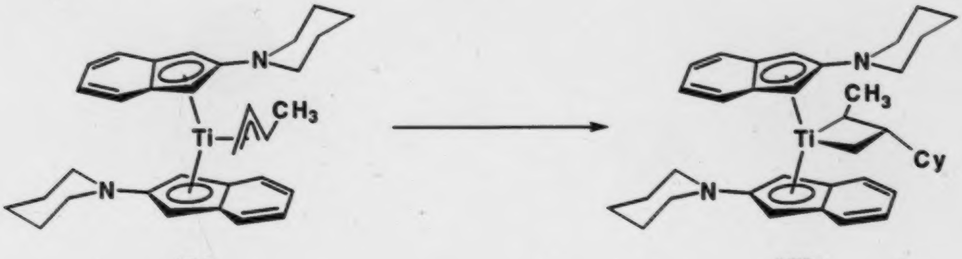
Titanacyclobutane 153b from Crotyl Complex 150:



150 153b

3-*tert*-Butyl -2-methyl bis(2'-piperidinoindenyl)titanacyclobutane 153b. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of bis(2'-piperidinoindenyl)titanium crotyl **150** (107 mg, 0.214 mmol) and SmI_2 (2.14 mL, 0.1 M in THF) was cooled to -35 °C. 2-Chloro-2-methylpropane (1 equivalent) was added to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 45 minutes. The solvent was removed *in vacuo* and the resulting red-brown residue was triturated with benzene and the solution filtered through a sintered-glass funnel layered with celite. Removal of benzene followed by crystallization in cold (-35 °C) diethyl ether yielded dark red-brown needles (42.0 mg, 36%). As a result of the thermal instability of titanacyclobutane **153b** only the ^{1}H NMR data is reported: ^{1}H NMR (360.1 MHz, C_6D_6): δ 7.46 (m, 1H, In), 7.33 (m, 3H, In), 7.02 (m, 1H, In), 6.89 (m, 2H, In), 6.80 (m, 1H, In), 5.66 (m, 1H, In), 5.60 (m, 1H, In), 4.76 (m, 1H, In), 4.46 (m, 1H, In), 2.86 (m, 4H, $CH_{2(piperidino)}$), 2.75 (m, 4H, $CH_{2(piperidino)}$), 2.23 (m, 1H, α-$C\underline{H}(CH_3)$), 1.81 (d, *J* = 6.5 Hz, 3H, α-$CH(C\underline{H}_3)$), 1.37 (m, 6H, $CH_{2((piperidino))}$), 1.26 (m, 6H, $CH_{2((piperidino))}$), 1.13 (s, 9H, $C(C\underline{H}_3)_3$), 0.11 (m, 1H, β-CH).

Titanacyclobutane 153c from Crotyl Complex 150:

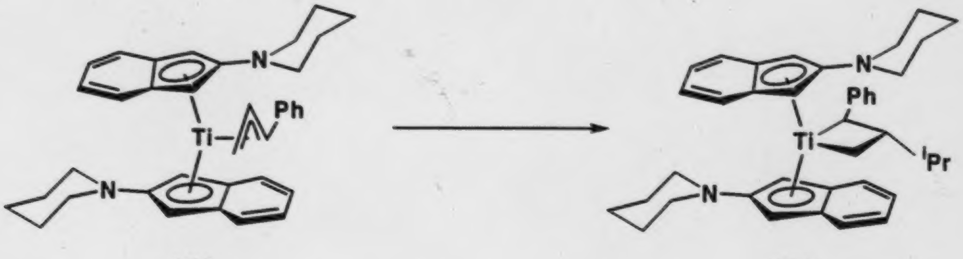


150　　**153c**

3-Cyclohexyl-2-methyl bis(2'-piperidinoindenyl)titanacyclobutane 153c. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of bis(2'-piperidinoindenyl)titanium crotyl **150** (108 mg, 0.2162 mmol) and SmI_2 (2.16 mL, 0.1 M in THF) was cooled to -35 °C. Cyclohexyl iodide (1 equivalent) was added to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 45 minutes. The solvent was removed *in vacuo* and the resulting red-brown residue was triturated with benzene and the solution filtered through a sintered-glass funnel layered with celite. Removal of benzene followed by crystallization in cold (-35 °C) diethyl ether yielded dark red-brown needles (88.0 mg, 70%). As a result of the thermal instability of titanacyclobutane **153c** only the ^{1}H NMR data is reported: ^{1}H NMR (400.1 MHz, C_6D_6): δ 7.43 (d, *J* = 7.8 Hz, 1H, In), 7.32 (dd, *J* = 8.6, 8.3 Hz, 1H, In), 7.19 (d, *J* =

8.0 Hz, 1H, In), 7.02 (dd, *J* = 7.7, 7.5 Hz, 1H, In), 6.93 (m, 3H, In), 6.86 (dd, *J* = 7.9, 7.2 Hz, 1H, In), 5.41 (d, *J* = 2.2 Hz, 1H, In), 5.25 (d, *J* = 2.2 Hz, 1H, In), 4.81 (d, *J* = 1.7 Hz, 1H, In), 4.68 (d, *J* = 1.7 Hz, 1H, In), 2.86 (m, 4H, $CH_{2(piperidino)}$), 2.73 (m, 4H, $CH_{2(piperidino)}$), 2.56 (t, *J* = 10.0 Hz, 1H, α-CH_2), 1.89 (d, *J* = 6.6 Hz, 3H, α-CH($C\underline{H}_3$)), 1.80 (m, 2H, α-$C\underline{H}(CH_3)$, $CH_{2(cy)}$), 1.37 (m, 6H, $CH_{2(piperidino)}$), 1.31 (m, 5H, $CH_{2(cy)}$), 1.26 (m, 6H, $CH_{2(piperidino)}$), 1.00 (m, 5H, $CH_{2(cy)}$), 0.39 (t, *J* = 10.0 Hz, 1H, α-CH_2), -0.24 (m, 1H, β-CH).

Titanacyclobutane 158a from Cinnamyl Complex 151:

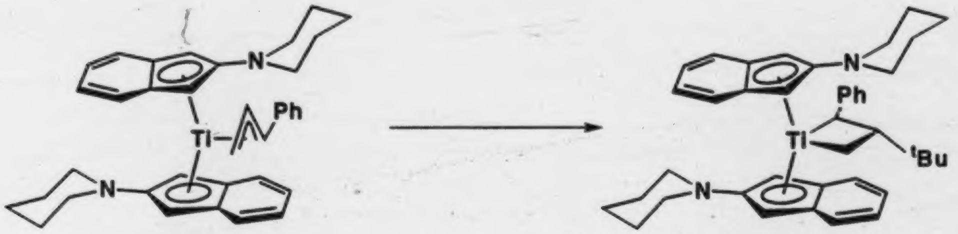


151 158a

3-Isopropyl-2-phenyl bis(2'-piperidinoindenyl)titanacyclobutane 158a. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of bis(2'-piperidinoindenyl)titanium cinnamyl **151** (31.0 mg, 0.0552 mmol) and SmI_2 (552 µL, 0.1 M in THF) was cooled to -35 °C. 2-Iodopropane (1 equivalent) was added to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 45 minutes. The solvent was removed *in vacuo* and the resulting red-brown residue was triturated with benzene and the solution filtered through a sintered-glass funnel layered with celite. Removal of benzene followed by crystallization in cold (-35 °C) diethyl ether layered with hexane yielded dark red-brown needles (24.0 mg, 72%). Spectroscopic and analytical data for titanacyclobutane **158a**: ^1H NMR (400.1 MHz,

C_6D_6, +70 °C): δ 7.36 (dd, J = 6.7, 1.0 Hz, 1H, In), 7.34 (dd, J = 8.8, 1.0 Hz, 1H, In), 7.30 (m, 1H, In), 7.23 (dd, J = 8.1, 7.3 Hz, 2H, $C_6\underline{H}_5$), 7.10 (d, J = 7.6 Hz, 2H, $C_6\underline{H}_5$), 7.05 (ddd, J = 7.7, 7.5, 1.0 Hz, 1H, In), 6.92 (m, 2H, In), 6.87 (d, J = 7.2 Hz, 1H, $C_6\underline{H}_5$), 6.73 (ddd, J = 7.7, 7.5, 1.1 Hz, 1H, In), 6.45 (dd, J = 8.4, 0.6 Hz, 1H, In), 5.40 (d, J = 2.3 Hz, 1H, In), 5.27 (d, J = 2.4 Hz, 1H, In), 5.03 (d, J = 2.1 Hz, 1H, In), 4.80 (d, J = 2.1 Hz, 1H, In), 2.91 (m, 3H, $CH_{2(piperidino)}$), 2.74 (m, 2H, $CH_{2(piperidino)}$), 2.61 (t, J = 10.0 Hz, 1H, α-CH_2), 2.49 (m, 1H, $CH_{2(piperidino)}$), 2.48 (d, J = 11.6 Hz, 1H, α-$C\underline{H}(C_6H_5)$), 1.54 (m, 1H, $C\underline{H}(CH_3)_2$), 1.35 (m, 14H, $CH_{2(piperidino)}$), 1.04 (d, J = 6.6 Hz, 3H, $CH(C\underline{H}_3)_2$), 0.95 (d, J = 6.6 Hz, 3H, $CH(C\underline{H}_3)_2$), 0.84 (m, 1H, β-CH), 0.04 (t, J = 10.0 Hz, 1H, α-CH_2). $^{13}C\{^1H\}$ (100.6 MHz, C_6D_6, APT): δ 156.3 ($In_{quaternary}$), 151.5 ($In_{quaternary}$), 127.6 ($Ph_{methine}$), 125.1 ($In_{methine}$), 124.7 ($In_{methine}$), 124.5 ($In_{methine}$), 124.2 ($In_{methine}$), 124.1 ($In_{methine}$), 123.0 ($In_{methine}$), 122.9 ($In_{methine}$), 122.7 ($In_{quaternary}$), 122.5 ($In_{methine}$), 121.9 ($In_{quaternary}$), 120.9 ($Ph_{methine}$), 118.3 ($In_{quaternary}$), 91.2 ($In_{methine}$), 90.1 ($In_{methine}$), 86.5 ($In_{methine}$), 86.5 (α-$\underline{C}H(C_6H_5)$), 82.7 (α-CH_2), 50.8 ($CH_{2(piperidino)}$), 49.5 ($CH_{2(piperidino)}$), 34.6 (β-CH), 27.4 ($\underline{C}H(CH_3)_2$), 25.8 ($CH_{2(piperidino)}$), 24.9 ($CH_{2(piperidino)}$), 24.5 ($CH_{2((piperidino))}$), 24.4 ($CH_{2(piperidino)}$), 23.8 ($CH(\underline{C}H_3)_2$) , 21.8 ($CH(\underline{C}H_3)_2$). Homonuclear decoupling experiments: Irr. δ 1.54: coupled to δ 1.04, 0.95, 0.04. Irr. δ 0.84: coupled to 2.67, 2.48, 1.54, 0.04. Irr. δ 0.04: coupled to δ 2.67, 2.48, 0.84. NOE difference spectrum (400.1 MHz, C_6D_6): Irr. at δ 7.10 (phenyl), enhancements at δ 5.40 (2.8%, indenyl), 4.80 (3.0%, indenyl), 2.49 (2.5%, piperidino), 0.84 (1.6%, β-CH), 0.04 (< 1.0%, α-CH_2). Irr. at δ 0.84 (β-CH), enhancements at δ 7.34 (7%, indenyl), 7.10 (7%, indenyl), 5.27 (3.0%, indenyl), 1.54 (<1.0%, $C\underline{H}(CH_3)_2$), 0.04 (2.0%, α-CH_2). IR (cm^{-1}, KBr, cast): 2933 (vs), 2853 (m), 2810 (m), 1585 (s), 1568 (vs), 1544 (m), 1511 (m), 1495 (m), 1487 (m), 1462 (s), 1449 (vs), 1385 (m), 1363 (m), 1275 (m), 1259 (m), 1193 (m), 1125 (m), 773 (s), 744 (s). Anal. Calcd for a diethyl ether adduct of complex **158a** ($C_{40}H_{48}TiN_2\cdot(C_2H_5)_2O$): C, 77.85; H, 8.61; N, 4.13. Found C, 77.74; H, 8.24; N, 4.57.

Titanacyclobutane 158b from Cinnamyl Complex 151:

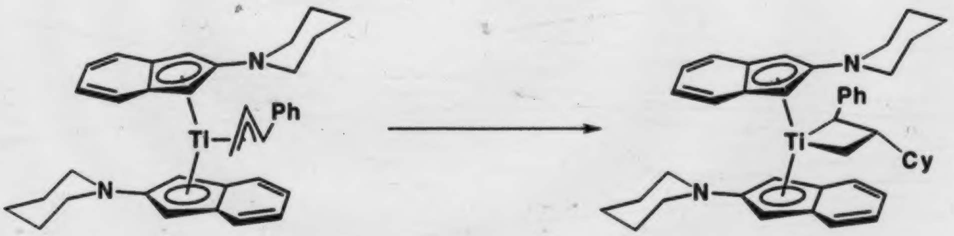


151 **158b**

3-*tert*-Butyl-2-phenyl bis(2'-piperidinoindenyl)titanacyclobutane 158b. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of bis(2'-piperidinoindenyl)titanium cinnamyl **151** (35.0 mg, 0.06232 mmol) and SmI_2 (623 µL, 0.1 M in THF) was cooled to -35 °C. 2-Chloro-2-methylpropane (1 equivalent) was added to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 2.5 h. The solvent was removed *in vacuo* and the resulting red-brown residue was triturated with benzene and the solution filtered through a sintered-glass funnel layered with celite. Removal of benzene followed by crystallization in cold (-35 °C) diethyl ether layered with hexane yielded dark red-brown needles (34.0 mg, 88%). Spectroscopic and analytical data for titanacyclobutane **158b**: ^{1}H NMR (400.1 MHz, C_6D_6, +70 °C): δ 7.41 (dd, *J* = 6.6, 2.0 Hz, 1H, In), 7.35 (d, *J* = 8.0 Hz, 1H, In), 7.33 (dd, *J* = 6.6, 2.4 Hz, 1H, In), 7.21 (brs, 2H, $C_6\underline{H}_5$), 7.15 (m, 1H, $C_6\underline{H}_5$), 6.99 (ddd, *J* = 7.2, 6.7, 1.0 Hz, 1H, In), 6.87 (m, 2H, In), 6.87 (m, 2H, $C_6\underline{H}_5$), 6.64 (ddd, *J* = 7.1, 6.8, 1.0 Hz, 1H, In), 6.14 (d, *J* = 8.4 Hz, 1H, In), 5.85 (d, *J* = 2.3 Hz, 1H, In), 5.51 (brs, 1H, In), 4.79 (brs, 1H, In), 4.71 (brs, 1H, In), 3.53 (d, *J* = 11.7 Hz, 1H, α-$C\underline{H}(C_6H_5)$), 2.95 (m, 4H, $CH_{2(piperidino)}$), 2.71 (t, *J* = 10.0 Hz, 1H, α-CH_2), 2.44 (brs, 2H, $CH_{2(piperidino)}$), 1.41 (m, 4H, $CH_{2(piperidino)}$), 1.32 (m, 10H, $CH_{2(piperidino)}$), 1.15 (m, 1H, β-CH), 1.03 (s, 9H, $C(C\underline{H}_3)_3$)), -0.24 (brs, 1H, α-CH_2). $^{13}C\{^1H\}$ (100.6 MHz, C_6D_6, APT): δ 156.5 ($In_{quaternary}$), 151.1 ($In_{quaternary}$), 128.1 ($In_{methine}$), 128.0

(Ph$_{methine}$), 127.9 (Ph$_{methine}$), 127.2 (In$_{methine}$), 127.2 (In$_{quaternary}$), 124.8 (In$_{methine}$), 124.5 (In$_{methine}$), 123.9 (In$_{methine}$), 123.4 (In$_{quaternary}$), 122.6 (In$_{methine}$), 122.4 (In$_{methine}$), 121.9 (In$_{quaternary}$), 121.9 (In$_{methine}$), 120.5 (Ph$_{methine}$), 118.9 (In$_{quaternary}$), 92.2 (In$_{methine}$), 90.9 (In$_{methine}$), 87.3 (In$_{methine}$), 81.6 (α-$\underline{C}H(C_6H_5)$), 80.7 (α-CH_2), 50.8 ($CH_{2(piperidino)}$), 49.5 ($CH_{2(piperidino)}$), 32.3 (β-CH), 29.9 ($C(\underline{C}H_3)_3$), 29.3 ($\underline{C}(CH_3)_3$), 25.7 ($CH_{2(piperidino)}$), 24.8 ($CH_{2(piperidino)}$), 24.6 ($CH_{2((piperidino))}$), 24.4 ($CH_{2(piperidino)}$). ^{13}C-^{1}H correlations (400.1 MHz, C_6D_6): δ 92.2 ↔ 5.85; 87.3 ↔ 4.79; 81.6 ↔ 3.53; 80.7 ↔ 2.71, - 0.24; 50.8 ↔ 2.95; 49.5 ↔ 2.44; 32.3 ↔ 1.15; 29.9 ↔ 1.03; 25.7 ↔ 1.32; 24.8 ↔ 1.41. IR (cm^{-1}, KBr, cast): 2935 (vs), 2898 (m), 2855 (s), 2810 (m), 1589 (s), 1543 (s), 1510 (s), 1496 (s), 1487 (s), 1471 (m), 1462 (m), 1448 (s), 1363 (s), 1257 (m), 1196 (m), 1123 (s), 977 (m), 792 (m), 772 (m), 740 (s), 700 (m). Anal. Calcd for a diethyl ether adduct of complex **158b** ($C_{41}H_{50}TiN_2$•$(C_2H_5)_2O$): C, 78.01; H, 8.73; N, 4.04. Found C, 78.32; H, 8.29; N, 4.46.

Titanacyclobutane 158c from Cinnamyl Complex 151:



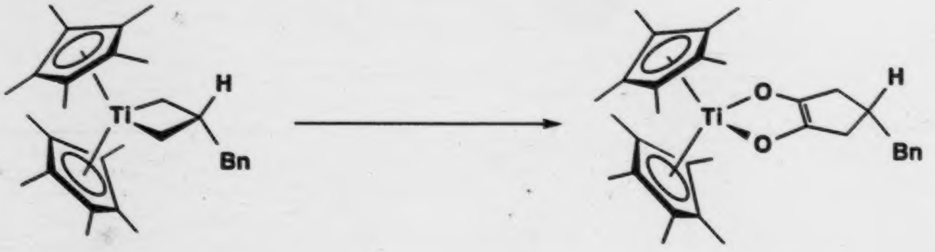
151 **158c**

3-Cyclohexyl-2-phenyl bis(2'-piperidinoindenyl)titanacyclobutane 158c. In the drybox, a 25 mL round bottom flask containing a THF solution (10 mL) of bis(2'-piperidinoindenyl)titanium cinnamyl **151** (31.0 mg, 0.0552 mmol) and SmI_2 (552 µL, 0.1 M in THF) was cooled to -35 °C. Cyclohexyl iodide (1 equivalent) was added to the cooled solution and the reaction mixture was allowed to warm to room temperature and stirred for 20 minutes. The solvent was removed *in vacuo* and the resulting red-brown residue was triturated with benzene and the solution filtered through a sintered-glass funnel layered with celite. Removal of benzene followed by crystallization in cold (-35 °C) diethyl ether layered with hexane yielded dark red-brown needles (28.0 mg, 80%). Spectroscopic and analytical data for titanacyclobutane **158c**: ^{1}H NMR (400.1 MHz, C_6D_6, +70 °C): δ 7.37 (d, *J* = 7.0 Hz, 1H, $C_6\underline{H}_5$), 7.36 (d, *J* = 7.8 Hz, 1H, In), 7.35 (dd, *J* = 7.8, 7.0 Hz, 1H, In), 7.31 (d, *J* = 7.7 Hz, 1H, In), 7.23 (dd, *J* = 7.6, 7.5 Hz, 1H, $C_6\underline{H}_5$), 7.10 (d, *J* = 7.7 Hz, 1H, $C_6\underline{H}_5$), 7.06 (dd, *J* = 8.9, 7.5 Hz, 1H, In), 6.90 (m, 2H, In), 6.87 (d, *J* = 7.2 Hz, 1H, $C_6\underline{H}_5$), 6.75 (dd, *J* = 7.6, 7.3 Hz, 1H, In), 6.47 (d, *J* = 8.3 Hz, 1H, In), 5.40 (d, *J* = 2.0 Hz, 1H, In), 5.26 (d, *J* = 2.1 Hz, 1H, In), 5.04 (brs, 1H, In), 4.78 (brs, 1H, In), 2.91 (m, 4H, $CH_{2(piperidino)}$), 2.74 (m, 3H, $CH_{2(piperidino)}$), 2.63 (t, *J* = 10.0 Hz, 1H, α-CH_2), 2.52 (m, 2H, $CH_{2(piperidino)}$), 2.41 (d, *J* = 11.1 Hz, 1H, α-$C\underline{H}(C_6H_5)$), 2.1 (m, 1H, $CH_{2(piperidino)}$), 2.03 (m, 1H, $CH_{2((piperidino)}$), 1.85 (m, 1H, CH_2(cy)), 1.70 (m, 6H, CH_2(cy)), 1.49 (m, 5H, CH_2(cy)), 1.31 (m, 8H, $CH_{2(piperidino)}$, CH_2(cy)), 0.80 (m, 1H, β-CH), 0.07 (t, *J* = 10.0 Hz, 1H, α-CH_2). ^{13}C (100.6 MHz, C_6D_6): δ 156.5 ($In_{quaternary}$), 151.4 ($In_{quaternary}$), 127.6 ($Ph_{methine}$), 125.2 ($In_{methine}$), 124.8 ($In_{methine}$), 124.6 ($In_{methine}$), 124.2 ($In_{methine}$), 124.1 ($In_{methine}$), 123.0 ($In_{methine}$), 122.9 ($In_{methine}$), 122.7 ($In_{quaternary}$), 122.5 ($In_{methine}$), 121.9 ($In_{quaternary}$), 120.9 ($Ph_{methine}$), 118.4 ($In_{quaternary}$), 90.9 ($In_{methine}$), 90.2 ($In_{methine}$), 86.5 ($In_{methine}$), 86.5 (α-$\underline{C}H(C_6H_5)$), 83.8 (α-CH_2), 50.9 ($CH_{2(piperidino)}$), 49.6 ($CH_{2(piperidino)}$), 45.3 (β-CH), 34.6 (CH_2(cy)), 33.0 (CH_2(cy)), 27.9 (CH_2(cy)), 27.8 (CH_2(cy)), 27.6 (CH_2(cy)), 26.4 (CH(cy)), 25.9 ($CH_{2(piperidino)}$), 24.9 ($CH_{2(piperidino)}$), 24.5 ($CH_{2(piperidino)}$), 24.4 ($CH_{2(piperidino)}$). IR (cm^{-1}, KBr, cast): 2931 (vs), 2850 (s), 1585 (m), 1568 (s), 1546 (m), 1462 (m), 1448 (s), 1385 (m), 1125 (m), 776 (m), 742 (s), 716 (m), 699 (m). Anal. Calcd for a diethyl ether adduct of complex **158c** ($C_{43}H_{52}TiN_2 \cdot C_4H_{10}O$): C, 78.5; H, 8.69; N, 3.9. Found C, 78.25; H, 8.58; N, 4.22.

CHAPTER 3. FUNCTIONALIZATION OF METALLACYCLOBUTANE COMPLEXES

3.2. Double Carbon Monoxide Insertion Reactions of Titanacyclobutane Complexes

Cyclopentenediolate Complex 179a from Titanacyclobutane 47a:

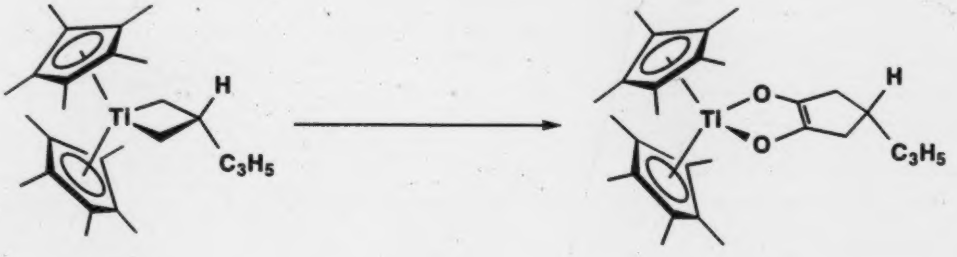


47a **179a**

Benzyl bis(pentamethylcyclopentadienyl)titanacyclopentenediolate 179a. In the drybox, the Fischer-Porter bottle was charged with a pentane solution (10 mL) of benzyl bis(pentamethylcyclopentadienyl)titanacyclobutane[25,42] **47a** (48.0 mg, 0.107 mmol) and then assembled. The sealed assembly was taken out of the dry box, cooled to -78 °C for 0.5 h and pressurized with CO (60 psig). After a further 0.5 h at this temperature, the cooling bath was removed and the reaction mixture allowed to warm to room temperature and stirred for an additional 2 h. The excess CO was then released and the assembly taken into the drybox where the resulting dark brown solution was concentrated and cooled to -35 °C, yielding a brown non-crystalline solid (47.0 mg, 88%). Spectroscopic and high resolution mass spectrometry data for complex **179a**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 7.1 (m, 5H, $CH_2C_6\underline{H}_5$), 2.73 (m, 2H, $C\underline{H}_2C_6H_5$), 2.60 (m, 4H, H-2, H-4), 1.80 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.74 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.25 (m, 1H, H-3). ^{13}C (100.6 MHz, C_6D_6, gated decoupled): δ 147.0 (s, Ti-$\underline{C}$=$\underline{C}$-), 141.9 (s, $CH_2\underline{C}_6H_{5ipso}$), 128.7 (d, J = 135 Hz, $CH_2\underline{C}_6H_5$), 128.6 (d, J = 140 Hz, $CH_2\underline{C}_6H_5$), 128.4 (d, J = 133 Hz, $CH_2\underline{C}_6H_5$), 121.9

(s, $\underline{C}_5(CH_3)_5$), 121.1 (s, $\underline{C}_5(CH_3)_5$), 44.1 (t, *J* = 128 Hz, $\underline{C}H_2C_6H_5$), 38.9 (t, *J* = 126 Hz, C-2(C-4)), 36.5 (d, *J* = 130 Hz, C-3), 11.6 (q, *J* = 126 Hz, $C_5(\underline{C}H_3)_5$), 11.5 (q, *J* = 126 Hz, $C_5(\underline{C}H_3)_5$). IR (cm^{-1}, KBr, pentane cast): 2976 (w), 2912 (m), 2850 (m), 2830 (m), 2817 (m), 1703 (w), 1600 (w), 1541 (m), 1494 (m), 1450 (m), 1438 (m), 1371 (s), 1333 (m), 1102 (s), 1077 (m), 1056 (m), 1024 (s), 748 (vs), 704 (vs), 663 (m). MS Calcd for $C_{32}H_{42}O_2Ti$ *m/e* 506.2661, found 506.2664.

Cyclopentenediolate Complex 179b from Titanacyclobutane 47b:

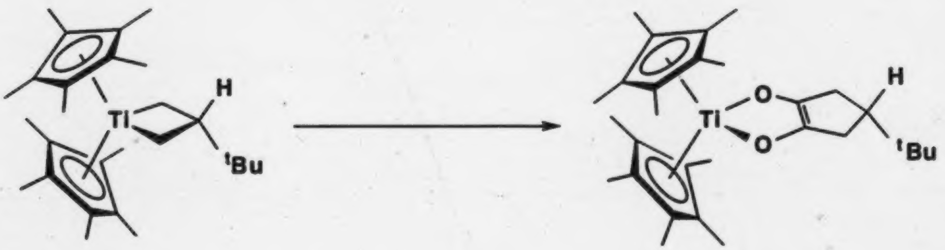


47b 179b

Allyl bis(pentamethylcyclopentadienyl)titanacyclopentenediolate 179b. In the drybox, the Fischer-Porter bottle was charged with a pentane solution (10 mL) of allyl bis(pentamethylcyclopentadienyl)titanacyclobutane[25,42] **47b** (70.0 mg, 0.174 mmol) and then assembled. The sealed assembly was taken out of the dry box, cooled to -78 °C for 0.5 h and pressurized with CO (60 psig). After a further 0.5 h at this temperature, the cooling bath was removed and the reaction mixture allowed to warm to room temperature and stirred for an additional 2 h. The excess CO was then released and the assembly taken into the drybox where the resulting dark brown solution was concentrated and cooled to -35 °C, yielding a brown non-crystalline solid (56.0 mg, 70%). Spectroscopic and high resolution mass spectrometry data for complex **179b**: ^1H NMR (360.1 MHz, C_6D_6): δ 5.88 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H, $CH_2C\underline{H}{=}CH_2$), 5.13 (dm, *J* = 17.1 Hz, 1H,

$CH_2CH=C\underline{H}_2$), 5.08 (dm, J = 10.2 Hz, 1H, $CH_2CH=C\underline{H}_2$), 2.72 (m, 2H, H-2(H-4)), 2.56 (m, 1H, H-3), 2.51 (m, 2H, H-2(H-4)), 2.29 (broad t, J = 6.7 Hz, 2H, $C\underline{H}_2CH=CH_2$), 1.85 (s, 15 H, $C_5(C\underline{H}_3)_5$), 1.83 (s, 15 H, $C_5(C\underline{H}_3)_5$). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6, APT): δ 147.0 (Ti-$\underline{C}$=$\underline{C}$-), 137.9 ($C_{olefinic}$), 122.0 ($\underline{C}_5(CH_3)_5$), 121.1 ($\underline{C}_5(CH_3)_5$), 115.5 ($C_{olefinic}$), 42.2 ($C_{methylene}$), 38.6 ($C_{methylene}$), 34.2 ($C_{methine}$), 11.6 ($C_5(\underline{C}H_3)_5$), 11.5 ($C_5(\underline{C}H_3)_5$). IR (cm^{-1}, KBr, pentane cast): 2974 (m), 2909 (m), 2856 (m), 2837 (m), 1707 (m), 1640 (m), 1595 (m), 1544 (m), 1492 (m), 1438 (m), 1376 (m), 1336 (m), 1263 (m), 1113 (m), 1083 (m), 1067 (m), 1020 (m), 992 (m), 910 (m), 804 (m), 790 (m), 728 (m), 692 (m), 666 (m). MS Calcd for $C_{28}H_{40}O_2Ti$ *m/e* 456.25076, found 456.25007.

Cyclopentenediolate Complex 179c from Titanacyclobutane 47e:

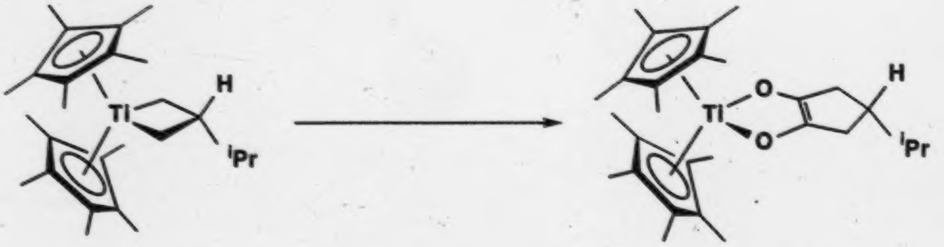


47e

179c

***tert*-Butyl bis(pentamethylcyclopentadienyl)titanacyclopentenediolate 179c**. In the drybox, the Fischer-Porter bottle was charged with a pentane solution (10 mL) of *tert*-butyl bis(pentamethylcyclopentadienyl)titanacyclobutane[25,42] **47e** (50.0 mg, 0.119 mmol) and then assembled. The sealed assembly was taken out of the dry box, cooled to -78 °C for 0.5 h and pressurized with CO (60 psig). After a further 0.5 h at this temperature, the cooling bath was removed and the reaction mixture allowed to warm to room temperature and stirred for an additional 2 h. The excess CO was then released and the assembly taken into the drybox where the resulting dark brown solution was concentrated and cooled to -35 °C, yielding a brown non-crystalline solid (43.0 mg, 75%). Spectroscopic and high resolution mass spectrometry data for complex **179c**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 2.52 (m, 5H, H-2, H-3, H-4), 1.80 (s, 30H, $C_5(C\underline{H}_3)_5$), 0.91 (s, 9H, $C(C\underline{H}_3)_3$). ^{13}C (100.6 MHz, C_6D_6, gated decoupled): δ 147.4 (s, Ti-$\underline{C}$=$\underline{C}$-), 121.8 (s, $\underline{C}_5(CH_3)_5$), 121.1 (s, $\underline{C}_5(CH_3)_5$), 45.8 (d, *J* = 126.7 Hz, C-3), 34.3 (t, *J* = 129.3 Hz, C-2(C-4)), 32.8 (s, $\underline{C}(CH_3)_3$), 27.2 (q, *J* = 124.2 Hz, $C(\underline{C}H_3)_3$), 11.6 (q, *J* = 126.3 Hz, $C_5(\underline{C}H_3)_5$), 11.2 (q, *J* = 126.3 Hz, $C_5(\underline{C}H_3)_5$). IR (cm^{-1}, KBr, pentane cast): 2956 (m), 2909 (m), 2864 (m), 1547 (w), 1481 (w), 1437 (m), 1379 (m), 1099 (w), 1065 (w), 1023 (m), 795 (w), 667 (w). MS Calcd for $C_{29}H_{44}O_2Ti$ *m/e* 472.28207, found 472.28075.

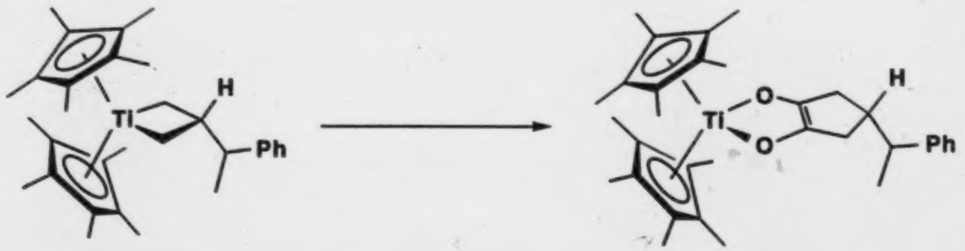
Cyclopentenediolate Complex 179d from Titanacyclobutane 47g:



47g 179d

Isopropyl bis(pentamethylcyclopentadienyl)titanacyclopentenediolate 179d. In the drybox, the Fischer-Porter bottle was charged with a pentane solution (10 mL) of isopropyl bis(pentamethylcyclopentadienyl)titanacyclobutane[25,42] **47g** (101 mg, 0.251 mmol) and then assembled. The sealed assembly was taken out of the dry box, cooled to -78 °C for 0.5 h and pressurized with CO (60 psig). After a further 0.5 h at this temperature, the cooling bath was removed and the reaction mixture allowed to warm to room temperature and stirred for an additional 2 h. The excess CO was then released and the assembly taken into the drybox where the resulting dark brown solution was concentrated and cooled to -35 °C, yielding a brown non-crystalline solid (95.0 mg, 83%). Spectroscopic and high resolution mass spectrometry data for complex **179d**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 2.54 (m, 4H, H-2(H-4)), 2.23 (m, *J* = 8.0, 8.5 Hz, 1H, H-3), 1.80 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.78 (s, 15H, $C_5(C\underline{H}_3)_5$) 1.56 (m, 1H, $C\underline{H}(CH_3)_2$), 0.92 (d, *J* = 6.0 Hz, 6H, $CH(C\underline{H}_3)_2$). ^{13}C (100.6 MHz, C_6D_6, gated decoupled): δ 147.5 (s, Ti-$\underline{C}$=$\underline{C}$), 121.9 (s, $\underline{C}_5(CH_3)_5$), 121.0 (s, $\underline{C}_5(CH_3)_5$), 42.7 (d, *J* = 123 Hz, C-3), 37.1 (t, *J* = 128 Hz, C-2(C-4)), 34.3 (d, *J* = 128 Hz, $\underline{C}H(CH_3)_2$), 20.7 (q, *J* = 124 Hz, $CH(\underline{C}H_3)_2$), 11.6 (q, *J* = 126 Hz, $C_5(\underline{C}H_3)_5$), 11.5 (q, *J* = 126 Hz, $C_5(\underline{C}H_3)_5$)). IR (cm^{-1}, KBr, pentane cast): 2960 (s), 2906 (vs), 2838 (s), 1558 (m), 1542 (s), 1490 (m), 1472 (m), 1464 (m), 1456 (m), 1436 (m), 1419 (m), 1374 (s), 1261 (s), 1089 (s), 1020 (s), 803 (s), 668 (m). MS Calcd for $C_{28}H_{42}O_2Ti$ *m/e* 458.26643, found 458.26642.

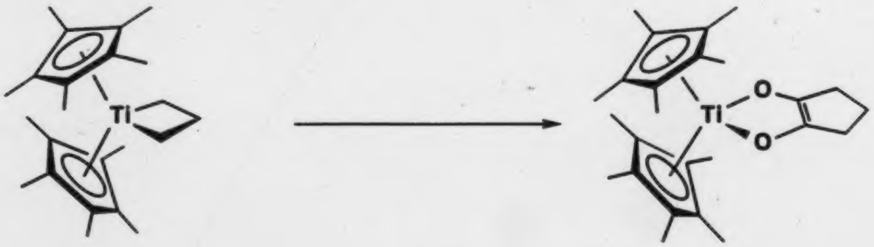
Cyclopentenediolate Complex 179i from Titanacyclobutane 47e:



47i   **179e**

Phenylethyl bis(pentamethylcyclopentadienyl)titanacyclopentenediolate 179e. In the drybox, the Fischer-Porter bottle was charged with a pentane solution (10 mL) of phenylethyl bis(pentamethylcyclopentadienyl)titanacyclobutane[25,42] **47i** (259 mg, 0.557 mmol) and then assembled. The sealed assembly was taken out of the dry box, cooled to -78 °C for 0.5 h and pressurized with CO (60 psig). After a further 0.5 h at this temperature, the cooling bath was removed and the reaction mixture allowed to warm to room temperature and stirred for an additional 2 h. The excess CO was then released and the assembly taken into the drybox where the resulting dark brown solution was concentrated and cooled to -35 °C, yielding a brown non-crystalline solid (260 mg, 90%). Spectroscopic and high resolution mass spectrometry data for complex **179e**: ^{1}H NMR (400 MHz, C_6D_6): δ 7.20 (m, 5H, $C_6\underline{H}_5$), 2.72 (m, 4H, H-2(H-4)), 2.49 (m, 1H, H-3), 2.35 (m, 1H, $CH_3(C\underline{H})C_6H_5$), 1.85 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.81 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.29 (d, *J* = 6.5 Hz, 3H, $CH(C\underline{H}_3)C_6H_5$). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, APT): δ 147.7 (Ti-$\underline{C}$=$\underline{C}$), 147.4 (Ti-$\underline{C}$=$\underline{C}$), 146.9 ($C_{quaternary}$, C_6H_{5ipso}), 128.6 ($\underline{C}_6H_5$), 128.0 ($\underline{C}_6H_5$, obscured by C_6D_6), 126.1 ($\underline{C}_6H_5$), 121.8 ($\underline{C}_5(CH_3)_5$), 121.0 ($\underline{C}_5(CH_3)_5$), 47.2 ($C_{methylene}$), 42.3 ($C_{methylene}$), 38.4 ($C_{methine}$), 37.8 ($C_{methine}$), 20.6 (C_{methyl}), 11.5 ($C_5(\underline{C}H_3)_5$), 11.5 ($C_5(\underline{C}H_3)_5$). IR (cm^{-1}, KBr, pentane cast): 3024 (m), 2960 (m), 2908 (m), 1706 (m), 1593 (m), 1543 (m), 1492 (m), 1451 (m), 1374 (m), 1328 (m), 1109 (m), 1082 (m), 1063 (m), 1022 (m), 804 (m), 761 (m), 700 (m), 666 (m). MS Calcd for $C_{33}H_{44}O_2Ti$ *m/e* 520.28210, found 520.28217.

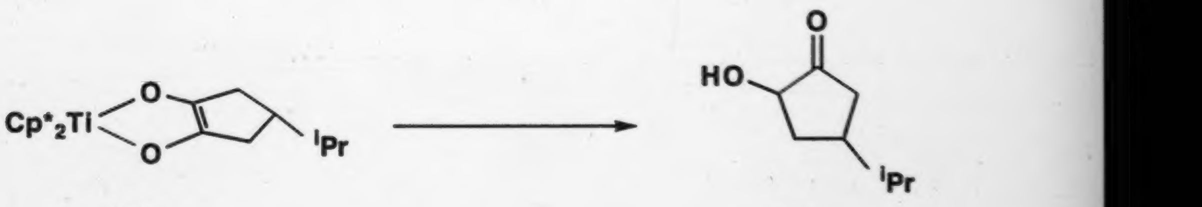
Cyclopentenediolate Complex 179f from Titanacyclobutane 47j:



47j **179f**

Bis(pentamethylcyclopentadienyl)titanacyclopentenediolate 179f. In the drybox, the Fischer-Porter bottle was charged with a pentane solution (10 mL) of bis(pentamethylcyclopentadienyl)titanacyclobutane[25,42] **47j** (156 mg, 0.434 mmol) and then assembled. The sealed assembly was taken out of the dry box, cooled to -78 °C for 0.5 h and pressurized with CO (60 psig). After a further 0.5 h at this temperature, the cooling bath was removed and the reaction mixture allowed to warm to room temperature and stirred for an additional 2 h. The excess CO was then released and the assembly taken into the drybox where the resulting dark brown solution was concentrated and cooled to -35 °C, yielding a brown non-crystalline solid (155 mg, 86%). Spectroscopic and high resolution mass spectrometry data for complex **179f**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 2.56 (t, *J* = 6.5 Hz, 4H, H-2(H-4)), 2.04 (m, 2H, H-3)), 1.77 (s, 30H, $C_5(C\underline{H}_3)_5$). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 147.9 (s, Ti-$\underline{C}$=$\underline{C}$), 121.4 (s, $\underline{C}_5(CH_3)_5$), 31.8 (t, *J* = 130.4 Hz, C-2(C-4)), 20.3 (t, *J* = 130.2 Hz, C-3), 11.5 (q, *J* = 126.3 Hz, $C_5(\underline{C}H_3)_5$). IR (cm^{-1}, KBr, pentane cast): 2909 (vs), 2861 (s), 2859 (s), 1539 (m), 1489 (m), 1437 (s), 1406 (m), 1376 (s), 1354 (m), 1338 (m), 1299 (m), 1141 (m), 1126 (m), 1068 (s), 1020 (m), 788 (m), 776 (m), 753 (m), 715 (m), 702 (m). MS Calcd for $C_{25}H_{36}O_2Ti$ *m/e* 416.21948, found 416.21974.

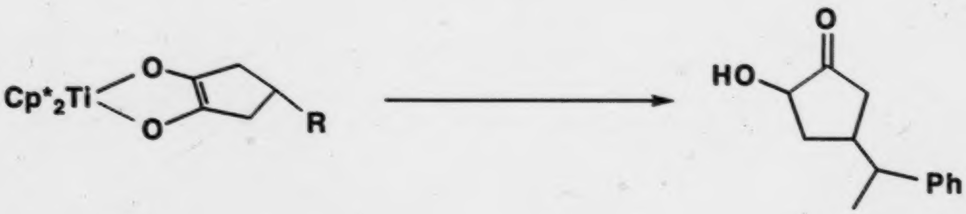
2-Hydroxy-4-isopropylcyclopentanone 180a from Cyclopentenediolate Complex 179d:



179d **180a**

2-Hydroxy-4-isopropylcyclopentanone 180a. In a Schlenk flask, pentenediolate complex **179a** (76.0 mg, 0.166 mmol) in pentane was treated with dry HCl (1 atmosphere) at room temperature. The resulting red-brown reaction mixture was stirred for a 20 minutes, after which the solvent was removed *in vacuo* to yield a red-brown residue. The residue was chromatographed on silica using hexane/ethyl acetate (3 : 1) as eluent and gave Cp*$_2$TiCl$_2$[223] (65.0 mg, quant.) and 2-Hydroxy-4-isopropylcyclopentanone **180a** (4.0 mg, 15%). Spectroscopic data (^{1}H NMR and infrared) for cyclopentanone **180a**: ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 4.13 (ddd, J = 11.8, 8.2, 2.4, 1H), 2.52 (m, 2H), 1.62 (m, 2H), 1.51 (m, 1H, $C\underline{H}(CH_3)_2$), 1.32 (m, 1H), 0.94 (d, J = 8.2 Hz, 3H, $CH(C\underline{H}_3)_2$), 0.92 (d, J = 8.2 Hz, 3H, $CH(C\underline{H}_3)_2$). IR (cm^{-1}, KCl, cast): 3440 (s, OH), 1737 (vs, C=O).

2-Hydroxycyclopentanone 180b from Cyclopentenediolate Complex 179e:

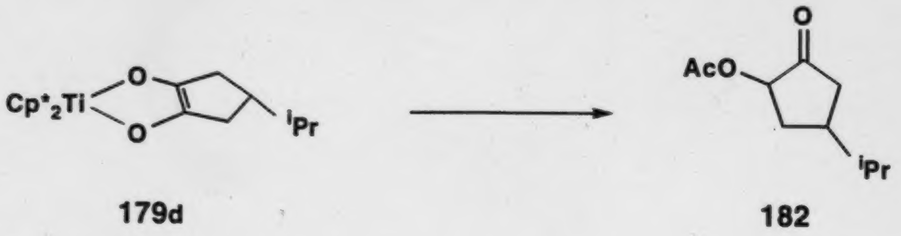


179e

180 b

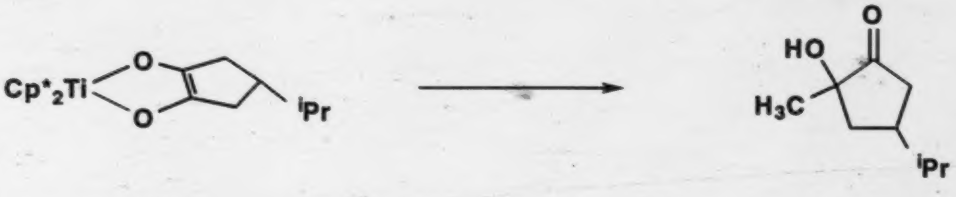
2-Hydroxy-4-(1-phenylethyl)cyclopentanone 180b. A THF solution (10 mL) of the pentenediolate (77.0 mg, 0.1479 mmol) in a 25 mL round bottom flask was placed under an atmosphere of nitrogen and cooled to 0 °C. Triflic acid (26.0 µL, 0.296) was added dropwise over two minutes and the reaction mixture was stirred for a further 13 minutes. The solvent was removed *in vacuo* and the violet residue triturated with diethyl ether and filtered through a short column of celite to yield a violet solid (bis(pentamethylcyclopentadienyl)titanium(di(aquo))bistriflate,[224,225] (80%) and a light brown filtrate. The filtrate was concentrated and chromatographed on preparative tlc using hexane/ethyl acetate (5 : 1) as eluant to yield a diastereomeric mixture of the 2-hydroxy-4-(1-phenylethyl)cyclopentanone **180b** (13.0 mg, 43%). Spectroscopic and high resolution mass spectrometry data for cyclopentanone **180b**: **Major diastereomer**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.30 (m, 2 H), 7.23 (m, 1 H), 7.17 (m, 2 H), 4.15 (ddd, *J* = 12.2; 8.2; 1.7 Hz, 1 H), 2.87 (brs, 1 H), 2.69 (m, 1 H), 2.57 (m, 1 H), 2.28 (m, 1 H), 2.19 (m, 1 H), 1.80 (dd, *J* = 19.3; 10.6 Hz, 1 H), 1.45 ("dd", *J* = 23.7; 11.9 Hz, 1 H), 1.33 (d, *J* = 6.9 Hz, 3 H). ^{13}C (100.6 MHz, $CDCl_3$, gated decoupled): δ 217.1 (s), 144.6 (s), 128.6 (d, *J* = 159.4 Hz), 127.2 (d, *J* = 138.1 Hz), 126.5 (d, *J* = 160.3 Hz), 76.5 (d, *J* = 140.6 Hz), 45.9 (d, *J* = 126.8 Hz), 40.1 (t, *J* = 130.6 Hz), 36.9 (d, *J* = 130.6 Hz), 36.3 (t, *J* = 132.1 Hz), 20.2 (q, *J* = 126.4 Hz). **Minor diastereomer**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.30 (m, 2 H), 7.23 (m, 1 H), 7.17 (m, 2 H), 4.04 (ddd, *J* = 12.2; 8.2; 1.7 Hz, 1 H), 2.49 (brs, 1 H), 2.69 (m, 1 H), 2.57 (m, 1 H), 2.17 (m, 1 H), 2.11 (m, 1 H), 1.99 (dd, *J* = 19.3; 10.6 Hz, 1 H), 1.29 (m, *J* = 23.7; 11.9 Hz, 1 H), 1.31 (d, *J* = 6.9 Hz, 3 H). ^{13}C (100.6 MHz, $CDCl_3$, gated decoupled): δ 216.9 (s), 145.2 (s), 128.5 (d, *J* = 159.4 Hz), 127.1 (d, *J* = 138.1 Hz), 126.5 (d, *J* = 160.3 Hz), 76.5 (d, *J* = 140.6 Hz), 45.9 (d, *J* = 126.8 Hz), 40.1 (t, *J* = 130.6 Hz), 37.2 (d, *J* = 130.6 Hz), 36.2 (t, *J* = 132.1 Hz), 19.8 (q, *J* = 126.4 Hz). IR (cm^{-1}, KCl, cast): 3443 (vs, OH), 3026 (vs), 2969 (vs), 2928 (vs), 2871 (vs), 1746 (vs, C=O), 1606 (m, C=C), 1493 (s), 1451 (s), 1106 (vs). MS Calcd for $C_{13}H_{16}O_2$ *m/e* 204.11504, found 204.11451.

2-Acetoxy-2-cyclopentanone 182 from Cyclopentenediolate Complex 179d:



2-Acetoxy-2-cyclopentanone 182. Cyclopentenediolate **179d** (540 mg, mmol) in pentane was treated with acetyl chloride (3 equivalents) and a few drops of pyridine at room temperature. The reaction mixture was stirred for 12 h during which time a red-brown material precipitated. Filtration through a short column of celite gave a dark red-brown residue ($Cp^*_2TiCl_2$,[223] quant.) and an orange filtrate. Removal of the solvent from the filtrate and purification of the resulting oil by chromatography on silica using 4% ethyl acetate in hexane as eluant gave 2-acetoxycyclopentanone **182** (43.0 mg, 20%). Spectroscopic and high resolution mass spectrometry data for compound **182**: ^{1}H NMR (300.1 MHz, C_6D_6): δ 4.99 (dd, J = 12.0, 8.0 Hz, 1H), 2.00 (m, 2H), 1.73 (s, 3H), 1.43 (dd, J = 18.7, 10.1 Hz, 1H), 1.13 (dd, J = 23.2, 11.6 Hz, 1H), 0.92 (m, 2H), 0.57 (d, J = 6.4 Hz, 3H), 0.51 (d, J = 6.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, APT): δ 211.0 (C=O), 170.2 (C=O), 76.6 ($C_{(methine)}$), 40.3 ($C_{(methylene)}$), 37.9 ($C_{(methylene)}$), 33.6 ($C_{(methine)}$), 33.2 ($C_{(methine)}$), 20.8 ($C_{(methyl)}$), 20.7 ($C_{(methyl)}$), 20.1 ($C_{(methyl)}$). IR (cm^{-1}, KCl, cast): 1757 (vs, C=O), 1739 (vs, C=O). MS Calcd for $C_{10}H_{16}O_3$ *m/e* 184.10994, found 184.10985.

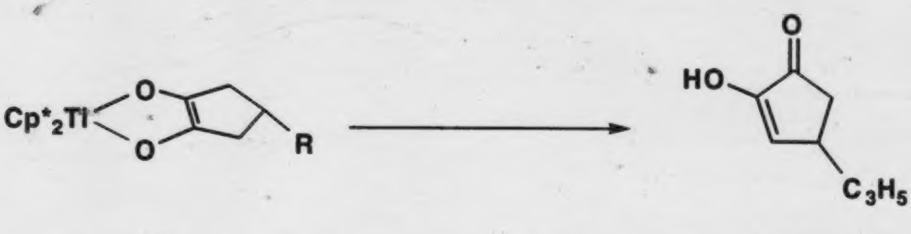
2-Hydroxy-2-methylcyclopentanone 185 from Cyclopentenediolate Complex 179d:



179d **185**

2-Hydroxy-3-isopropyl-2-methylcyclopentanone 185. In a Schlenk flask, 3-isopropyl bis(pentamethylcyclopentadienyl)titanacyclopentenediolate **179d** (54.0 mg, 0.118 mmol) in pentane (10 mL) was treated with methyllithium (170 µL, 1 M in diethyl ether) at room temperature. The reaction mixture was allowed to stir for 4 h, after which the solvents were removed *in vacuo*. The Schlenk flask was taken into the drybox where the resulting yellow residue was triturated with pentane and filtered through a sintered-glass funnel to give a yellow pentane-soluble material, ($Cp^*{}_2Ti(CH_3)_2$,[84,216] (38.0 mg, 92%)) and a white residue (dilithium pentenediolate, 15.0 mg (84%)). The latter material was suspended in diethyl ether (5 mL) in a Schlenk flask and then treated with excess methyl iodide at room temperature. After 2 h at this temperature, the reaction was quenched with water (5 mL) and the organic layer separated and dried with $MgSO_4$. The solvent was removed *in vacuo* and the oily residue chromatographed on silica using hexane/ethyl acetate (3 : 1) as eluant. Compound **185** was obtained as a pale yellow oil (5.0 mg, 25%). Spectroscopic (^1H NMR and infrared) and mass spectrometry data for compound **185**: ^1H NMR (360.1 MHz, $CDCl_3$): δ 2.53 (m, 2H), 2.20 (m, 2H), 1.75 (m, 1H), 1.59 (s, 1H, OH), 1.47 (m, 1H), 1.26 (s, 3H), 0.96 (d, J = 6.4 Hz, 3H), 0.93 (d, J = 6.5 Hz, 3H). IR (cm^{-1}, KCl, cast): 3415 (vs), 2959 (vs), 2927 (vs), 2869 (m), 1745 (vs), 1458 (m), 1368 (m), 1138 (m), 1073 (m). MS Calcd for $C_9H_{16}O_2$ *m/e* 156.11503, found (low resolution) 156.1. Important fragment ions include: *m/e* 113.1 (40%, M^+-C_3H_7), 58.1 (100%), 43 (78%, C_3H_7).

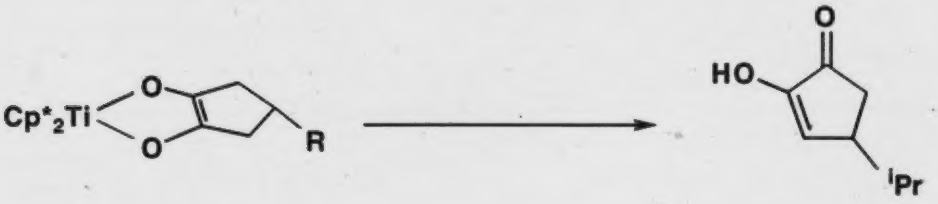
2-Hydroxy-2-cyclopentenone 186a from Cyclopentenediolate Complex 179b:



179b **186a**

4-Allyl-2-hydroxy-2-cyclopentenone 186a. In two 25 mL round bottom flasks, THF solutions of the allyl bis(pentamethyl-cyclopentadienyl)titanacyclopentenediolate **179b** (56.0 mg, 0.1218 mmol) and triphosgene (36.0 mg, 0.1218 mmol) were cooled to 0 °C for 20 minutes. The cooled enediolate solution was added to the triphosgene solution dropwise over 5 minutes during which time a vigorous reaction took place. The reaction mixture was stirred at this temperature for 1 h and then allowed to warm to room temperature. After 1 h at this temperature, the THF was removed *in vacuo* to yield a red-brown oily residue. The residue was triturated with hexane and the solution filtered through a short column of celite to give a pale yellow-orange filtrate and a dark red residue ($Cp^*{}_2TiCl_2$,[223] 32.0 mg (67%). Removal of the hexane from the filtrate and purification on silica (hexane/ether, 4 : 1) yielded the 2-hydroxy-2-cyclopentenone as an off-white solid (16.0 mg, 95%). Spectroscopic and high resolution mass spectrometry for compound **186a**: ^1H NMR (360.1 MHz, $CDCl_3$): δ 6.51 (d, J = 2.9 Hz, 1H), 5.78 (m, 1H), 5.45 (s, 1H, OH), 5.08 (m, 2H), 2.89 (m, 1H), 2.60 (dd, J = 19.4, 5.9 Hz, 1H), 2.25 (m, 2H), 2.11 (dd, J = 19.4, 1.6 Hz, 1H). ^{13}C (100.6 MHz, $CDCl_3$, gated decoupled): δ 203.1 (s, *C*=O), 152.5 (s, C=$\underline{C}$(OH)), 135.1 (d, J = 154 Hz, =$\underline{C}H_{\text{olefinic}}$), 132.5 (d, J = 165 Hz, =$\underline{C}H_{\text{olefinic}}$), 117.5 (t, J = 156 Hz, C=CH_2), 39.6 (t, J = 121 Hz, $C_{\text{methylene}}$), 38.3 (t, J = 132 Hz, $C_{\text{methylene}}$), 34.0 (d, J = 136 Hz, C_{methine}). IR (cm^{-1}, KCl, cast): 3350 (m, OH), 3082 (w), 2913 (w), 1703 (vs, C=O), 1648 (m, C=C), 1634 (m, C=C), 1395 (s), 1198 (m), 1099 (s). MS Calcd for $C_8H_{10}O_2$ *m/e* 138.06808, found 138.06771.

2-Hydroxy-2-cyclopentenone 186b from Cyclopentenediolate Complex 179d:

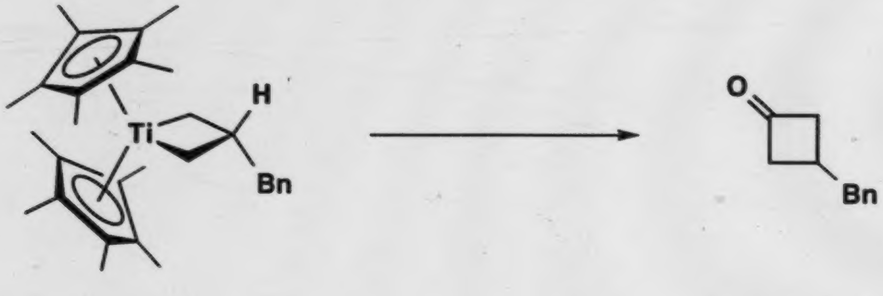


179d **186b**

4-Isopropyl-2-hydroxy-2-cyclopentenone 186b.[192] In two 25 mL round bottom flasks, THF solutions of the isopropyl bis(pentamethylcyclopentadienyl)-titanacyclopentenediolate **179d** (120 mg, 0.2617 mmol) and triphosgene (81.0 mg, 0.2617 mmol) were cooled to 0 °C for 20 minutes. The cooled enediolate solution was added to the triphosgene solution dropwise over 5 minutes, during which time a vigorous reaction took place. The reaction mixture was stirred at this temperature for 1 h and then allowed to warm to room temperature. After 1 h at this temperature, the THF was removed *in vacuo* to yield a red-brown oily residue. The residue was triturated with hexane and the solution filtered through a short column of celite to give a pale yellow-orange filtrate and a dark red residue ($Cp^*_2TiCl_2$)[223]. Removal of the hexane and purification on silica (hexane/ether, 4 : 1) yielded the 2-hydroxy-2-cyclopentenone **186b** as an off-white solid (30.0 mg, 82%). Spectroscopic (^{1}H NMR and infrared) and high resolution mass spectrometry for compound **186b**: ^{1}H NMR (360.1 MHz, $CDCl_3$): δ 6.53 (d, *J* = 2.9 Hz, 1H), 5.35 (s, 1H, OH), 2.64 (m, 1H), 2.60 (dd, *J* = 19.4, 5.9 Hz, 1H), 2.11 (dd, *J* = 19.4, 1.6 Hz, 1H), 1.69 (m, 1H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H). IR (cm^{-1}, KCl, cast): 3335 (m, OH), 2962 (m), 2871 (m), 1704 (vs, C=O), 1655 (m, C=C), 1634 (m, C=C), 1394 (s). MS Calcd for $C_8H_{12}O_2$ *m/e* 140.08372, found 140.08399.

3.3. Single Carbon Monoxide Insertion Reactions of Titanacyclobutane Complexes

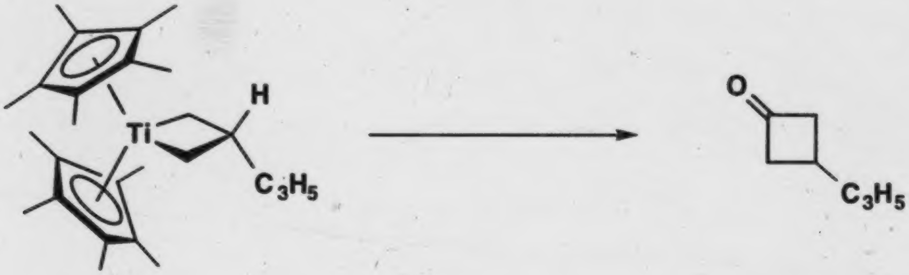
Benzylcyclobutanone 189a from Titanacyclobutane 47a:



47a **189a**

3-Benzylcyclobutanone 189a.[197] In the drybox, the Fischer-Porter bottle was charged with the benzyl bis(pentamethylcyclopentadienyl)titanacyclobutane[25,42] **47a** (27.0 mg, 0.0606 mmol) and pentane (5 mL) and then assembled. The sealed assembly was taken out of the dry box and heated to 45 °C for 15 minutes. The reaction vessel was then pressurized with CO (10 psig) and the reaction mixture stirred for 12 h at this temperature. The excess CO was vented and the assembly taken into the drybox where the yellow-orange solution was concentrated and cooled (-35 °C) to precipitate out $Cp^*_2Ti(CO)_2$,[73,193,194] (19.0 mg, 85%). The solvent was removed *in vacuo* from the mother liquor to yield cyclobutanone **189a** (8.0 mg, 85 %). Spectroscopic and high resolution mass spectrometry data for compound **189a**: ^1H NMR (300.1 MHz, C_6D_6): δ 7.32 (m, 2H, $CH_2C_6\underline{H}_5$), 7.20 (m, 3H, $CH_2C_6\underline{H}_5$), 3.12 (m, 2H, H-2(H-4)), 2.91 (d, *J* = 7.2 Hz, 2H, $C\underline{H}_2C_6H_5$), 2.77 (m, 3H, H-2(H-4), H-3). IR (cm^{-1}, KBr, film): 2918 (w), 1778 (s, C=O), 1499 (w), 1450 (w), 1384 (w), 736 (m), 703 (m). MS Calcd for $C_{11}H_{12}O$ *m/e* 160.08882, found 160.08859.

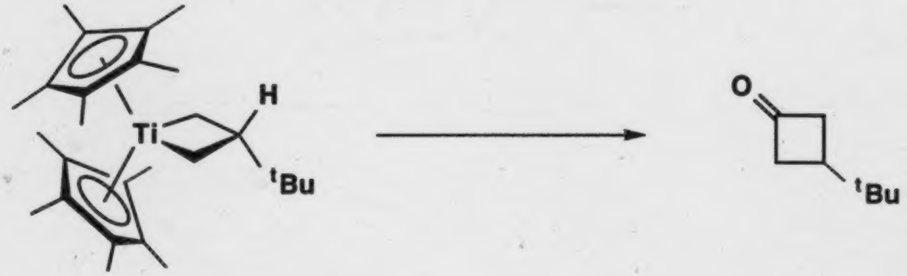
Allylcyclobutanone 189b from Titanacyclobutane 47b:



47b **189b**

3-Allylcyclobutanone 189b. In the drybox, the Fischer-Porter bottle was charged with the allyl bis(pentamethylcyclopentadienyl)titanacyclobutane[25,42] **47b** (25.0 mg, 0.0629 mmol) and pentane (5 mL) and then assembled. The sealed assembly was taken out of the drybox and heated to 45 °C for 15 minutes. The reaction vessel was then pressurized with CO (10 psig) and the reaction mixture stirred for 12 h at this temperature. The excess CO was vented and the assembly taken into the drybox where the yellow-orange solution was transferred to a reaction bomb. The volatiles were vacuum transferred (using a high vacuum line) to another reaction bomb leaving a yellow-orange residue of the $Cp^*{}_2Ti(CO)_2$,[73,193,194] (20.0 mg, 85%). The yield was determined by gas chromatography (3.0 mg, 45 %) using 2-butanone as a standard. For spectroscopic analysis the reaction was carried out in benzene-d_6. Spectroscopic and mass spectrometry data for compound **189b**: ^1H NMR (400.1 MHz, C_6D_6): δ 5.44 (m, 1H, $CH_2{=}C\underline{H}$), 4.83 (m, 2H, $C\underline{H_2}{=}CH$), 2.60 (m, 2H, $CH_2{=}CHC\underline{H_2}$), 2.22 (m, 2H, α-$CH_2$), 1.75 (brs, 3H, α-$CH_2$, β-CH). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 204.9 (s, $\underline{C}{=}O$), 136.2 (d, J = 150.6 Hz, $CH_2{=}\underline{C}HCH_2$), 116.0 (t, J = 155.4 Hz, $\underline{C}H_2{=}CHCH_2$), 52.0 (t, J = 133.8 Hz, C-2), 23.0 (d, J = 139.3 Hz, C-3), 22.7 (t, J = 126.5 Hz, $CH_2{=}CH\underline{C}H_2$). IR ($cm^{-1}$, gas phase): 2945 (w), 1808 (s, C=O), 1641 (w), 1395 (w), 1005 (w), 996 (w), 921 (w). Retention time (GC) 6.99 mins. MS Calcd for $C_7H_{10}O$, m/e 110.07317, found (low resolution) 110 (2, M^+), 95 (2), 67 (100), 53 (50), 39 (62).

tert-Butylcyclobutanone 189c from Titanacyclobutane 47c:

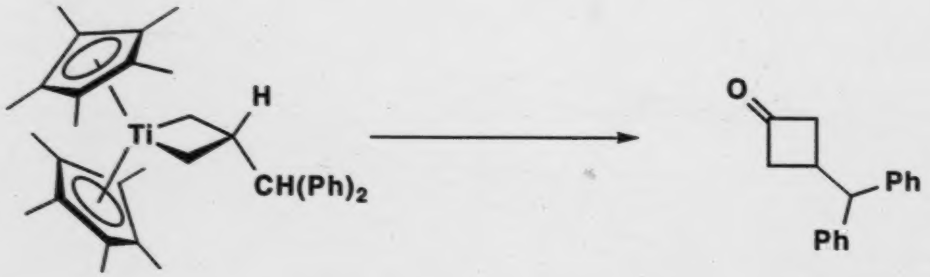


47c **189c**

3-*tert*-Butylcyclobutanone 189c.[199] In the drybox the Fischer-Porter bottle was charged with the *tert*-butyl bis(pentamethylcyclopentadienyl)titanacyclobutane[25,42] **47c** (21.0 mg, 0.0489 mmol) and pentane (5 mL) and then assembled. The sealed assembly was taken out of the drybox and heated to 45 °C for 15 minutes. The reaction vessel was then pressurized with CO (10 psig) and the reaction mixture stirred for 12 h at this temperature. The excess CO was vented and the assembly taken into the drybox where the yellow-orange solution was transferred to a reaction bomb. The volatiles were vacuum transferred (using a high vacuum line) to another reaction bomb leaving a yellow-orange residue of the $Cp^*{}_2Ti(CO)_2$,[73,193,194] (18.0 mg, quant.). The yield was determined by gas chromatography (6.0 mg, quant.) using 2-butanone as a standard. For spectroscopic analysis the reaction was carried out in benzene-d_6. Spectroscopic and high resolution mass spectrometry data for compound **189c**: ^1H NMR (400.1 MHz, C_6D_6): δ 2.44 (apparent doublet, $J = 8.3$ Hz, 4H, H-2(H-4)), 1.65 (m, 1H, H-3), 0.59 (s, 9H, $C(C\underline{H}_3)_3$). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 204.6 (s, $\underline{C}$=O), 47.7

(t, *J* = 132.9 Hz, C-2(C-4)), 34.8 (d, *J* = 136.4 Hz, C-3), 31.2 (s, $\underline{C}(CH_3)_3$), 26.2 (q, *J* = 126.2 Hz, $C(\underline{C}H_3)_3$). IR (cm^{-1}, gas phase): 2965 (m), 1804 (s, C=O), 1474 (w), 1377 (w), 1203 (w), 1094 (w). Retention time (GC) 7.91 mins. MS Calcd for $C_8H_{14}O$ *m/e* 126.10446, found 126.10456.

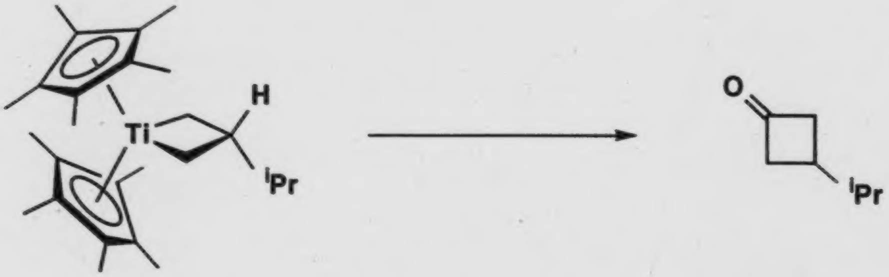
Diphenylmethylcyclobutanone 189d from Titanacyclobutane 47d:



47d **189d**

3-Diphenylmethylcyclobutanone 189d. In the drybox, the Fischer-Porter bottle was charged with the diphenylmethyl bis(pentamethylcyclopentadienyl)titanacyclobutane[25,42] **47d** (124 mg, 0.235 mmol) and pentane (10 mL) and then assembled. The sealed assembly was taken out of the dry box and heated to 45 °C for 15 minutes. The reaction vessel was then pressurized with CO (10 psig) and the reaction mixture stirred for 12 h at this temperature. The excess CO was vented and the assembly taken into the drybox where the yellow-orange solution was concentrated and cooled (-35 °C) to precipitate out $Cp^*{}_2Ti(CO)_2$,[73,193,194] (88 mg, quant.). The solvent was removed *in vacuo* from the mother liquor to yield cyclobutanone **189d** (131 mg, 91%). Spectroscopic (^1H NMR and infrared) and high resolution mass spectrometry data for compound **189d**: ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.25 (m, 10H, $CH(C_6\underline{H}_5)_2$), 3.91 (d, *J* = 10.7 Hz, 1H, C$\underline{H}(C_6H_5)_2$), 3.16 (m, 3H, H-2(H-4), H-3), 2.81 (m, 2H, H-2(H-4)). IR (cm^{-1}, film): 3026 (w), 2927 (w), 1781 (s, C=O), 1598 (w), 1493 (m), 1451 (m), 1373 (m), 1106 (m), 755 (w), 741 (w), 698 (m). MS Calcd for $C_{17}H_{16}O$ *m/e* 236.12012, found 236.12041.

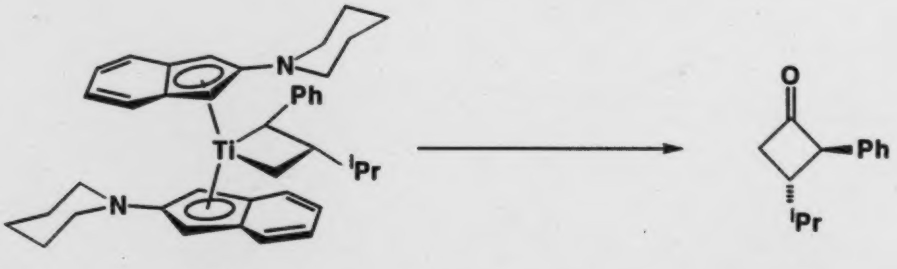
Isopropylcyclobutanone 189e from Titanacyclobutane 47g:



47g **189e**

3-Isopropylcyclobutanone 189e.[199,226] In the drybox the Fischer-Porter bottle was charged with the isopropyl bis(pentamethylcyclopentadienyl)titanacyclobutane[25,42] **47g** (21.0 mg, 0.0528 mmol) and pentane (5 mL) and then assembled. The sealed assembly was taken out of the drybox and heated to 45 °C for 15 minutes. The reaction vessel was then pressurized with CO (10 psig) and the reaction mixture stirred for 12 h at this temperature. The excess CO was vented and the assembly taken into the drybox where the yellow-orange solution was transferred to a reaction bomb. The volatiles were vacuum transferred (using a high vacuum line) to another reaction bomb leaving a yellow-orange residue of the $Cp^*_2Ti(CO)_2$,[73,193,194] (20.0 mg, quant.). The yield was determined by gas chromatography (6.0 mg, quant.) using 2-butanone as a standard. For spectroscopic analysis the reaction was carried out in benzene-d_6. Spectroscopic and high resolution mass spectrometry data for compound **189e**: ^{1}H NMR (300.1 MHz, C_6D_6): δ 2.57 (m, 2H, H-2(H-4)), 2.27 (m, 2H, H-2(H-4)), 1.40 (m, 1H, H-3), 1.05 (m, 1H, $C\underline{H}(CH_3)_2$), 0.60 (d, J = 6.6 Hz, 6H, $CH(C\underline{H}_3)_2$). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 204.6 (s, $\underline{C}$=O), 50.8 (t, J = 133.4 Hz, C-2(C-4)), 33.9 (d, J = 123.2 Hz, $\underline{C}H(CH_3)_2$), 31.6 (d, J = 132.9 Hz, C-3), 20.3 (q, J = 126.0 Hz, $CH(\underline{C}H_3)_2$). IR (cm^{-1}, gas phase): 2968 (m), 1805 (s, C=O), 1470 (w), 1368 (w), 1096 (w). Retention time (GC) 6.68 mins. MS Calcd for $C_7H_{12}O$ *m/e* 112.0881, found 112.08862

3-Isopropyl-2-phenylcyclobutanone 190a from Titanacyclobutane 158a:

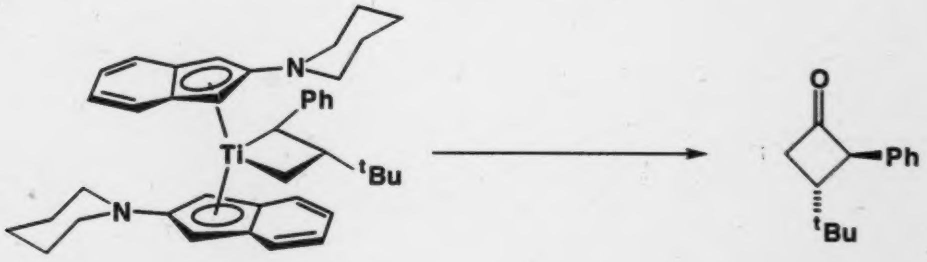


158a **190a**

3-Isopropyl-2-phenylcyclobutanone 190a. In the drybox, the Fischer-Porter bottle was charged with titanacyclobutane complex **158a** (34.0 mg, 0.0557 mmol) and toluene (5 mL) and then assembled. The assembly was taken out of the drybox and heated to 45 °C for 15 minutes. The reaction vessel was then pressurized with CO (10 psig) and the reaction mixture stirred for 6 h at this temperature. The excess CO was vented and the assembly taken into the drybox where the opaque violet colored solution was filtered through a short column of celite to give a dark brown residue and a violet filtrate. Removal of the solvent *in vacuo* and purification of the residue on silica using 5% ethyl acetate in hexane gave cyclobutanone **190a** (10.0 mg, quant.). Spectroscopic (^1H NMR and infrared) and high resolution mass spectrometry data for compound **190a**: ^1H NMR (360.1 MHz, $CDCl_3$): δ 7.32 (dd, J = 7.1, 6.8 Hz, 2H), 7.23 (m, 3H), 4.08 (dt, J = 8.1, 2.4

Hz, 1H), 3.07 (ddd, J = 17.4, 8.8, 2.2 Hz, 1H), 2.85 (ddd, J = 17.4, 8.1, 2.2 Hz, 1H), 2.34 (m, 1H), 1.85 (m, 1H), 1.03 (d, J =6.6 Hz, 3H), 1.00 (d, J = 6.0 Hz, 3H). IR (cm^{-1}, KBr, film): 1781 (C=O). MS Calcd for $C_{13}H_{16}O$ *m/e* 188.12012, found 188.11973.

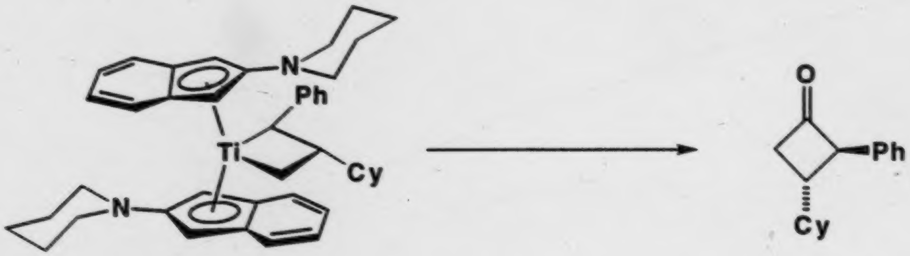
3-*tert-Butyl*-2-phenylcyclobutanone 190b from Titanacyclobutane 158b:



158b **190b**

3-*tert*-Butyl-2-phenylcyclobutanone 190b. In the drybox, the Fischer-Porter bottle was charged with titanacyclobutane complex **158b** (29.0 mg, 0.0469 mmol) and toluene (5 mL) and then assembled. The assembly was taken out of the drybox and heated to 45 °C for 15 minutes. The reaction vessel was then pressurized with CO (10 psig) and the reaction mixture stirred for 6 h at this temperature. The excess CO was vented and the assembly taken into the drybox where the opaque violet colored solution was filtered through a short column of celite to give a dark brown residue and a violet filtrate. Removal of the solvent *in vacuo* and purification of the residue on silica using 5% ethyl acetate in hexane gave cyclobutanone **190b** (10.0 mg, quant.). Spectroscopic (^{1}H NMR and infrared) and high resolution mass spectrometry data for compound **190b**: ^{1}H NMR (360.1 MHz, $CDCl_3$): δ 7.32 (m, 2H), 7.21 (m, 3H), 4.11 (ddd, J = 8.0, 2.5, 2.3 Hz, 1H), 2.97 (ddd, J = 19.1, 9.7, 3.0 Hz, 1H), 2.90 (ddd, J = 19.1, 9.6, 3.0 Hz, 1H), 2.54 (m, 1H), 1.01 (s, 9H). IR (cm^{-1}, KBr, film): 1781 (C=O). MS Calcd for $C_{14}H_{18}O$ *m/e* 202.13577, found 202.13545.

3-Cyclohexyl-2-phenylcyclobutanone 190c from Titanacyclobutane 158c:

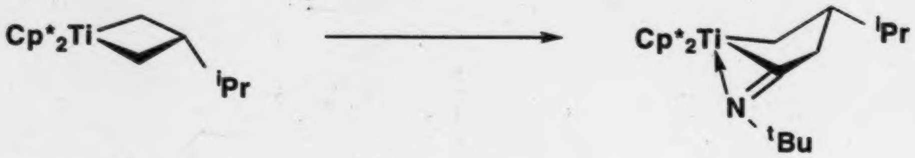


158c **190c**

3-Cyclohexyl-2-phenylcyclobutanone 190c. In the drybox, the Fischer-Porter bottle was charged with titanacyclobutane complex **158c** (87.0 mg, 0.1349 mmol) and toluene (5 mL) and then assembled. The assembly was taken out of the drybox and heated to 45 °C for 15 minutes. The reaction vessel was then pressurized with CO (10 psig) and the reaction mixture stirred for 6 h at this temperature. The excess CO was vented and the assembly taken into the drybox where the opaque violet colored solution was filtered through a short column of celite to give a dark brown residue and a violet filtrate. Removal of the solvent *in vacuo* and purification of the residue on silica using 5% ethyl acetate in hexane gave cyclobutanone **190c** (30.0 mg, quant.). Spectroscopic (^{1}H and ^{13}C NMR) and high resolution mass spectrometry data for compound **190c**: ^{1}H NMR (360.1 MHz, $CDCl_3$): δ 7.32 (dd, *J* = 7.6, 7.0 Hz, 2H), 7.21 (m, 3H), 4.11 (ddd, *J* = 8.0, 2.5, 2.3 Hz, 1H), 3.06 (ddd, *J* = 17.3, 8.7, 2.4 Hz, 1H), 2.85 (ddd, *J* = 17.3, 8.7, 2.4 Hz, 1H), 2.35 (m, 1H), 1.81 (m, 4H), 1.50 (m, 4H), 1.26 (m, 2H), 1.01 (m, 1H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, APT): δ 206.7 ($C_{(quaternary)}$, $\underline{C}$=O), 136.6 ($C_{(quaternary)}$), 128.6 ($C_{(methine)}$), 127.5 ($C_{(methine)}$), 126.9 ($C_{(methine)}$), 68.9 ($C_{(methine)}$), 48.4 ($C_{(methylene)}$), 44.8 ($C_{(methine)}$), 38.0 ($C_{(methine)}$), 31.6 ($C_{(methylene)}$), 31.1 ($C_{(methylene)}$), 26.3 ($C_{(methylene)}$), 26.2 ($C_{(methylene)}$), 26.0 ($C_{(methylene)}$). MS Calcd for $C_{16}H_{20}O$ *m/e* 228.15141, found 228.15102.

3.4. Isonitrile Insertion Reactions of Titanacyclobutane Complexes

Iminoacyl Complex 191a from Titanacyclobutane 47g:

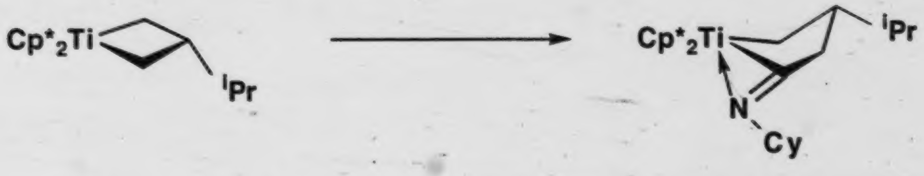


47g **191a**

2-*tert*-Butylimino-4-isopropylbis(pentamethylcyclopentadienyl)titanacyclopentane 191a. In a Schlenk flask, isopropyl bis(pentamethylcyclopentadienyl)titanacyclobutane complex **47g** (24.0 mg, 0.584 mmol) in toluene (5 mL) was cooled to -78 °C. *tert*-Butylisonitrile (7 µL, 0.584 mmol) was added to the cooled solution. The cooling bath was removed and the reaction mixture allowed to warm to room temperature and stirred for 1 h. Removal of the solvent *in vacuo* yielded a dark brownish-green air sensitive solid. This material was recrystallized from a hexane solution cooled to - 35 °C to yield brownish-green cubes (26.0 mg, 92%). Spectroscopic and analytical data for complex **191a**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 2.69 (m, 1H, α-CH_2), 1.97 (m, 1H, N=C-C$\underline{H}_2$), 1.79 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.75 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.74 (m, 1H, N=C-C$\underline{H}_2$; N=C-$CH_2C\underline{H}$), 1.26 (s, 9H, $C(C\underline{H}_3)_3$), 1.26 (m, 1H, $C\underline{H}(CH_3)_2$), 1.01 (d, *J* = 6.8 Hz, 3H, $CH(C\underline{H}_3)_2$), 0.98 (d, *J* = 6.7 Hz, 3H, $CH(C\underline{H}_3)_2$), -1.15 (m, 1H, α-CH_2). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 233.8 (s, $\underline{C}$=N), 121.1 (s, $\underline{C}_5(CH_3)_5$), 66.4 (dt, *J* = 121.6, 11.1 Hz, α-CH_2), 57.2 (s, $\underline{C}(CH_3)_3$), 48.6 (t, *J* = 122.9 Hz, $\underline{C}H_2C$=N), 44.2 (d, *J* = 124.0 Hz, $\underline{C}H(CH_3)_2$), 37.3 (d, *J* = 122.1 Hz, N=C-$CH_2\underline{C}H$), 31.3 (q, *J* = 124.9 Hz, $C(\underline{C}H_3)_3$), 21.3 (q, *J* = 122.9 Hz, $CH(\underline{C}H_3)_2$), 20.9 (q, *J* = 122.9 Hz, $CH(\underline{C}H_3)_2$), 12.6 (q, *J* = 126.1 Hz, $C_5(\underline{C}H_3)_5$), 12.3 (q, *J* = 126.1 Hz, $C_5(\underline{C}H_3)_5$). Homonuclear decoupling experiments: Irr. δ 2.69: coupled to δ 1.74, -1.15. Irr. δ 1.97: coupled to 1.74. Irr. δ 1.74:

2.69, 1.97, 1.26, -1.14. Irr. δ 1.26: coupled to 1.01, 0.98. Irr. δ - 1.15: coupled to 2.69, 1.74. IR (cm^{-1}, KBr, cast): 2960 (vs), 2904 (vs), 2865 (vs), 1588 (s, C=N), 1542 (w), 1494 (m), 1457 (s), 1377 (s), 1357 (s), 1218 (m), 1185 (s), 1164 (w), 1143 (w), 1076 (w), 1064 (w), 1020 (m), 985 (w), 791 (m), 740 (m), 709 (w). Anal Calcd for $C_{31}H_{51}NTi$ C, 76.67; H, 10.59; N, 2.88. Found C, 76.62; H, 10.68; N, 2.95.

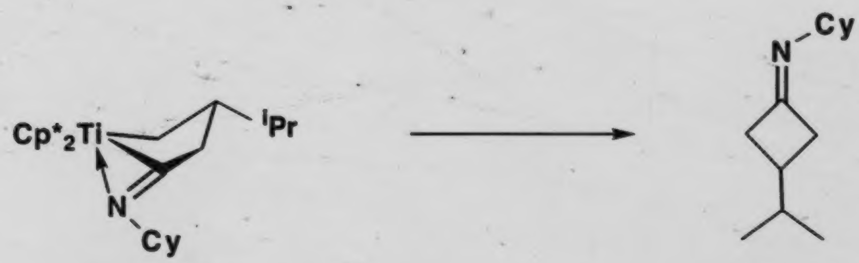
Iminoacyl Complex 191b from Titanacyclobutane 47g:



47g **191b**

2-cyclohexylimino-4-isopropylbis(pentamethylcyclopentadienyl)titanacyclopentane 191b. In a Schlenk flask, isopropyl bis(pentamethylcyclopentadienyl)titanacyclobutane complex **47g** (36.0 mg, 0.0887 mmol) was cooled to -78 °C. Cyclohexylisonitrile (11 µL, 0.887 mmol) was added to the cooled solution. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Removal of the solvent *in vacuo* yielded a dark brownish-green air sensitive solid. This material was recrystallized from a hexane solution cooled to - 35 °C to yield brownish-green cubes (41.0 mg, 90%). Spectroscopic and analytical data for complex **191b**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 3.26 (m, 1H, $C\underline{H}$(cy)), 2.75 (ddd, J = 15.3, 5.4, 3.4 Hz, 1H, α-CH_2), 2.05 (m, 1H, N=C-$CH_2C\underline{H}$), 1.80 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.77 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.65 (m, 8H, $C\underline{H}_2$(cy); N=C-$C\underline{H}_2$CH), 1.28 (m, 5H, $C\underline{H}_2$(cy); $C\underline{H}(CH_3)_2$), 0.99 (d, J = 6.8 Hz, 3H, $CH(C\underline{H}_3)_2$), 0.96 (d, J = 6.6 Hz, 3H, $CH(C\underline{H}_3)_2$), -1.20 (ddd, J = 11.0, 4.4, 4.0 Hz, 1H, α-CH_2). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 234.2 (s, $\underline{C}$=N), 121.3 (s, $\underline{C}_5(CH_3)_5$), 121.2 (s, $\underline{C}_5(CH_3)_5$), 67.1 (dt, J = 122.0, 10.6 Hz, α-CH_2), 60.6 (d, J = 130.3 Hz, C$\underline{H}$(cy)), 44.7 (dt, J = 121.0, 9.4 Hz, N=C$\underline{C}H_2$), 43.5 (d, J = 121.4 Hz, $\underline{C}H(CH_3)_2$), 37.5 (d, J = 126.6 Hz, N=C-$CH_2\underline{C}H$), 35.5 (t, J = 126.0 Hz, $\underline{C}H_2$(cy)), 34.4 (t, J = 124.0 Hz, $\underline{C}H_2$(cy)), 26.6 (t, J = 125.4 Hz, $\underline{C}H_2$(cy)), 26.0 (t, J = 126.4 Hz, $\underline{C}H_2$(cy)), 25.9 (t, J = 126.4 Hz, $\underline{C}H_2$(cy)), 21.3 (q, J = 123.3 Hz, $CH(\underline{C}H_3)_2$), 20.7 (q, J = 122.6 Hz, $CH(\underline{C}H_3)_2$), 12.6 (q, J = 126.2 Hz, $C_5(\underline{C}H_3)_5$), 12.2 (q, J = 126.0 Hz, $C_5(\underline{C}H_3)_5$). Homonuclear decoupling experiments: Irr. δ 2.75: coupled to δ 2.05, - 1.20. Irr. δ -1.20: coupled to 2.75, 2.05. IR (cm^{-1}, KBr, cast): 2954 (vs), 2925 (vs), 2853 (vs), 1709 (w), 1567 (s, C=N), 1494 (m), 1448 (s), 1378 (s), 1362 (m), 1344 (m), 1301 (m), 1289 (m), 1260 (m), 1162 (m), 1148 (m), 1072 (m), 1022 (s), 991 (m), 791 (m). Anal Calcd for $C_{33}H_{53}NTi$ C, 77.46; H, 10.44; N, 2.74. Found C, 77.51; H, 10.68; N, 2.83.

Cycylobutanimine 192 from Iminoacyl Complex 191b:



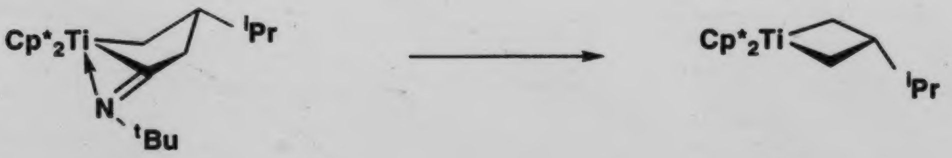
191b

192

N-[(3-isopropyl)-1-cyclobutylidene]-1-cyclohexylamine 192.[212] In the drybox, a Fischer-Porter bottle was charged with a benzene solution (1 mL) of the η^2-cyclohexyliminoacyl complex **191b** (20.5 mg, 0.04 mmol) and assembled. The sealed assembly was pressurized with ethylene (10 psig) and heated to 65°C for 12 h. The color of the reaction mixture changed from green to brown during this time. The Fischer-Porter bottle was vented and taken into the drybox and the solvent removed *in vacuo*.

The residue was dissolved in minimum hexane and cooled to -35 °C, yielding Cp^*_2Ti(ethylene)[227] as a brownish-yellow solid (12.5 mg, 90%). Removal of the solvent yielded cyclobutanimine **192** (7.0 mg, 94%) as an oil. Carbon monoxide or diphenylacetylene is also useful for trapping the Ti(II) species, but the reaction is less efficient. The reaction was done in benzene-d_6 for NMR purposes. Spectroscopic and high resolution mass spectrometry data for compound **192**: ^{1}H NMR (360.1 MHz, C_6D_6): δ 3.14 (septet, J = 4.5 Hz, 1H, N-C$\underline{H}$(cy)), 2.84 (ddt, J = 16.3, 8.8, 3.0 Hz, 1H, H-2(H-4)), 2.61 (ddt, J = 14.6, 8.7, 3.0 Hz, 1H, H-2(H-4)), 2.44 (ddd, J = 16.4, 6.4, 3.0, 1H, H-2(H-4)), 2.17 (dddd, 16.1, 6.8, 3.0, 1.0 Hz, 1H, H-2(H-4)), 2.15(m, 10H, CH_2(cy)), 1.28 (m, 1H, C$\underline{H}$(CH_3)$_2$), 0.73 (d, J = 6.6 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 0.70 (d, J = 6.6 Hz, 3H, CH(C$\underline{H}_3$)$_2$). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 200.7 (s, $\underline{C}$=N), 69.2 (t, J = 148 Hz, C-2(C-4)), 67.8 (t, J = 148 Hz, C-2(C-4)), 60.6 (d, J = 136.7 Hz, N$\underline{C}$H(cy)), 42.1 (t, J = 134.0 Hz, $\underline{C}H_2$(cy)), 38.1 (t, J = 133.2 Hz, $\underline{C}H_2$(cy)), 35.3 (d, J = 135.0 Hz, C-3), 34.4 (t, J = 128.0 Hz, $\underline{C}H_2$(cy)), 34.2 (d, J = 121 Hz, $\underline{C}$H(CH_3)$_2$), 26.2 (t, J = 123.3 Hz, $\underline{C}H_2$(cy)), 25.1 (t, J = 124.5 Hz, $\underline{C}H_2$(cy)), 20.1 (q, J = 125.4 Hz, CH($\underline{C}H_3$)$_2$), 20.0 (q, J = 125.4 Hz, CH($\underline{C}H_3$)$_2$). IR (cm^{-1}, KBr, cast): 2956 (s), 2926 (vs), 2853 (s), 1708 (m, C=N), 1448 (m), 1377 (m), 1365 (m), 1114 (m), 1022 (m), 791 (m), 724 (m). MS Calcd $C_{13}H_{23}N$ *m/e* 193.18304, found 193.18395.

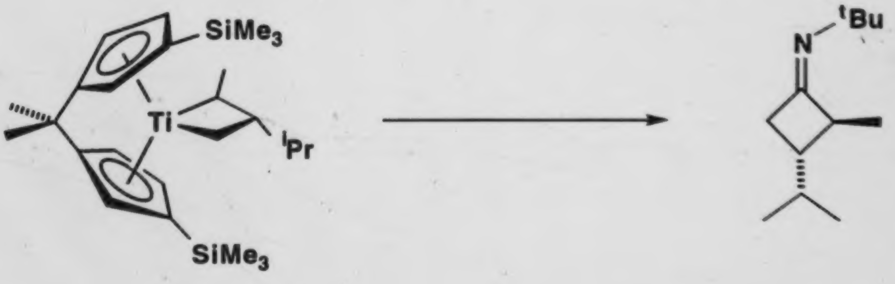
Thermolysis of 2-*tert*-Butylimino-4-isopropylbis(pentamethylcyclopentadienyl) titanacyclopentane 191a:



191a **43g**

A benzene-d_6 solution of *tert*-butyliminoacyl complex **191a** (26.0 mg, 0.0537 mmol) was heated for 23 h at 70 °C during which time the color of the reaction mixture changed from brownish-green to red-brown. ^{1}H NMR analysis of the red-brown residue obtained after removal of the solvent indicated the presence of 3-isopropyl bis(pentamethylcyclopentadienyl)titanacyclobutane **47g**.[39,42] Recrystallization of the red-brown residue using hexane cooled to -35 °C yielded needles (21.0 mg, quant.). A ^{1}H NMR spectrum of a benzene-d_6 solution of this material (5 mg) with 1 mg of an authentic sample of complex **47g** confirms its identity.

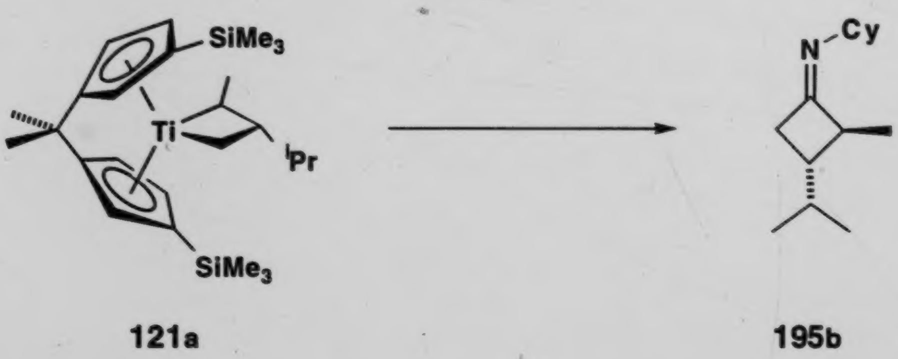
Cycylobutanimine 195a from *ansa*-[1]-titanacyclobutane 121a:



121a **195a**

N-[(3-isopropyl-2-methyl)-1-cyclobutylidene]-1-*tert*-butylamine 195a. In a 25-mL Schlenk flask, 3-isopropyl-2-methyl *ansa*-[1]-{dimethylmethano bis(3,3'-trimethylsilylcyclopentadienyl)}titanacyclobutane **121a** (28.0 mg, 0.061 mmol) in toluene (5 mL) was cooled to -78 °C. One equivalent each of the *tert*-butylisonitrile (9 μL) and diphenylacetylene (14.0 mg) was added to the cooled solution and after 0.5 h at this temperature, cooling was stopped and the reaction mixture allowed to warm to room temperature and stirred for a further 1.5 h. The solvent was removed *in vacuo* and the resulting residue triturated with hexane and the solution filtered through a short column of celite. Removal of the hexane gave cyclobutanimine **195a** (10.0 mg, 80%). The organometallic template was not recovered even in the presence of excess (> 2 equivalents) diphenylacetylene or keeping the reaction mixture at low temperature for a longer time. Spectroscopic (^{1}H and infrared) and high resolution mass spectrometry data for compound **195a**: ^{1}H NMR (360.1 MHz, C_6D_6): δ 2.76 (ddd, J = 15.1, 7.4, 1.5 Hz, 1H, H-4), 2.60 (m, 1H, H-2), 2.27 (dd, J = 15.1, 7.4, 1H, H-4), 1.50 (m, 1H, H-3), 1.26 (s, 9H, C(C$\underline{H}_3$)$_3$), 1.22 (d, J = 7.0 Hz, 3H, CH(C$\underline{H}_3$)), 0.80 (m, 1H, C$\underline{H}$(CH$_3$)$_2$), 0.77 (d, J = 6.2 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 0.74 (d, J = 6.2 Hz, 3H, CH(C$\underline{H}_3$)$_2$). IR (cm^{-1}, KBr, cast): 2956 (s), 1725 (w, C=N), 1465 (w), 1366 (w), 1247 (s), 839 (vs), 790 (vs). MS Calcd for $C_{12}H_{23}N$ *m/e* 181.18304, found 181.18363.

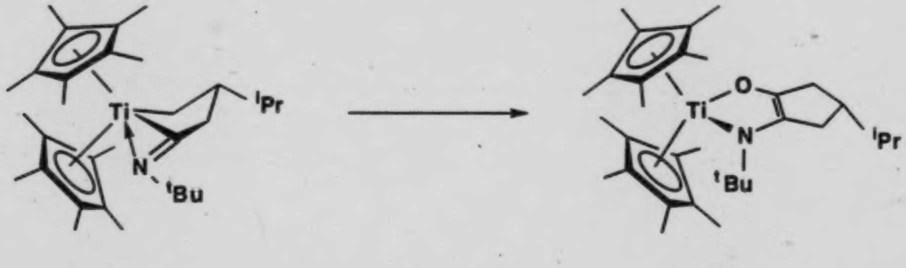
Cycylobutanimine 195b from Titanacyclobutane 121a:



N-[(3-isopropyl-2-methyl)-1-cyclobutylidene]-1-cyclohexylamine 195b. In a 25-mL Schlenk flask, 3-isopropyl-2-methyl *ansa*-[1]-{dimethylmethano bis(3,3'-trimethylsilylcyclopentadienyl)}titanacyclobutane **121a** (28.0 mg, 0.061 mmol) in toluene (5 mL) was cooled to -78 °C. Cyclohexylisonitrile (10 μL, 0.061 mmol) and diphenylacetylene (14.0 mg, 0.061 mmol) was added to the cooled solution and after 0.5

h at this temperature, cooling was stopped and the reaction mixture allowed to warm to room temperature and stirred for a further 1.5 h. The solvent was removed *in vacuo* and the resulting residue triturated with hexane and the solution filtered through a short column of celite. Removal of the hexane from the filtrate to gave cyclobutanimine **195b** (10.0 mg, 90%). The organometallic template was not recovered even in the presence of excess (>2 equivalents) diphenylacetylene or keeping the reaction mixture at low temperature for a longer time. Spectroscopic and high resolution mass spectrometry data for compound **195b**: ^{1}H NMR (300.1 MHz, C_6D_6): δ 3.15 (septet, J = 4.7 Hz, 1H, N-$\mathrm{C\underline{H}}$), 2.63 (m, 2H, H-2(H-4), 2-CH_3), 2.04 (dd, J = 15.4, 7.5 Hz, 1H, H-4), 1.70 (m, 5H, $\mathrm{\underline{C}H_2}$(cy)), 1.55 (m, 1H, H-3), 1.27 (m, 5H, $\mathrm{\underline{C}H_2}$(cy)), 1.23 (d, J = 6.0 Hz, 3H, $\mathrm{CH(C\underline{H}_3)}$), 0.85 (m, 1H, $\mathrm{C\underline{H}(CH_3)_2}$), 0.77 (d, J = 6.4 Hz, 3H, $\mathrm{CH(C\underline{H}_3)_2}$), 0.75 (d, J = 6.4 Hz, 3H, $\mathrm{CH(C\underline{H}_3)_2}$). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 200.6 (s, $\mathrm{\underline{C}{=}N}$), 60.2 (d, J = 129.1 Hz, $\mathrm{C{=}N\underline{C}H}$(cy)), 50.6 (d, J = 127 Hz, 2-$\mathrm{\underline{C}H(CH_3)}$), 44.7 (d, J = 135 Hz, C-3), 36.4 (t, J = 134 Hz, C-2(C-4)), 34.8 (d, J = 124.2 Hz, $\mathrm{\underline{C}H(CH_3)_2}$), 34.6 (t, J = 127.6 Hz, $\mathrm{\underline{C}H_2}$(cy)), 34.5 (t, J = 127.6 Hz, $\mathrm{\underline{C}H_2}$(cy)), 26.2 (t, J = 124.7 Hz, $\mathrm{\underline{C}H_2}$(cy)), 25.1 (t, J = 128.7 Hz, $\mathrm{\underline{C}H_2}$(cy)), 25.0 (t, J = 128.7 Hz, $\mathrm{\underline{C}H_2}$(cy)), 20.6 (q, J = 128.6 Hz, $\mathrm{CH(\underline{C}H_3)_2}$), 20.4 (q, J = 128.6 Hz, $\mathrm{CH(\underline{C}H_3)_2}$), 17.0 (q, J = 125.6 Hz, 2-$\mathrm{CH(\underline{C}H_3)}$). IR (cm^{-1}, KBr, cast): 2956 (s), 2827 (s), 2857 (m), 1711 (m, C=N), 1464 (m), 1451 (m), 1247 (s), 839 (vs), 797 (s), 755 (m). MS Calcd for $C_{14}H_{25}N$ *m/e* 207.19870, found 207.19790.

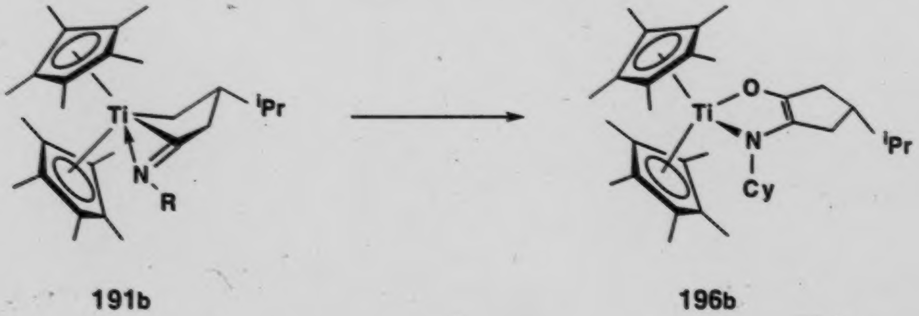
Titanocene Amidoenolate 196a from Iminoacyl Complex 191a:



191a **196a**

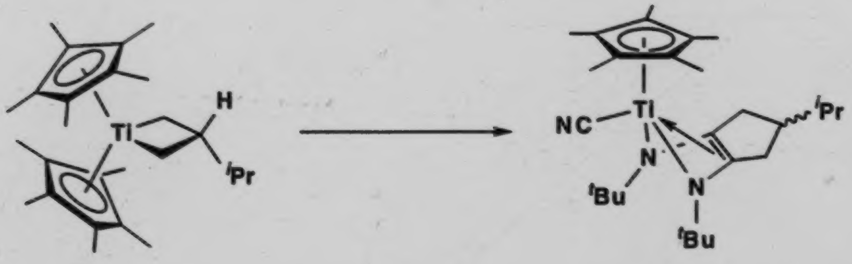
Isopropylbis(pentamethylcyclopentadienyl)titanacyclobutane-(*tert*-butylamido) enolate 196a. In the drybox, a Fischer-Porter bottle was charged with a toluene solution (10 mL) of iminoacyl complex **191a** (61.0 mg, 0.126 mmol) and assembled. The sealed vessel was taken out of the drybox and the solution cooled to -78°C for 0.5 h. The vessel was then pressurized with CO (60 psig) and the reaction mixture allowed to warm slowly to room temperature over a period of 10 h. The excess CO was vented from the reaction vessel and it was then taken into the drybox where the toluene solution was removed *in vacuo*. The residue was dissolved in 0.5 mL of pentane and cooled to -35°C to yield dark brown needles (60.0 mg, 93%). Spectroscopic and high resolution mass spectrometry data for complex **196a**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 2.67 (m, 1H, $C\underline{H}_2$), 2.49 (m, 1H, $C\underline{H}_2$), 2.32 (m, 1H, $C\underline{H}_2$), 2.01 (m, 1H, $C\underline{H}_2$), 1.86 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.84 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.61 (m, 1H, $CH_2)_2C\underline{H}$), 1.36 (s, 9H, $C(C\underline{H}_3)_3$), 1.23 (m, 1H, $C\underline{H}(CH_3)_2$), 1.01 (d, J = 6.6 Hz, 3H, $CH(C\underline{H}_3)_2$), 0.98 (d, J = 6.5 Hz, 3H, $CH(C\underline{H}_3)_2$). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 142.5 (s, $O\underline{C}=C$), 122.5 (s, $\underline{C}_5(CH_3)_5$), 122.4 (s, $\underline{C}_5(CH_3)_5$), 115.9 (s, $N-\underline{C}=C$), 50.6 (s, $\underline{C}(CH_3)_3$), 39.8 (t, J = 125.9 Hz, $OC=C(N)\underline{C}H_2$), 36.9 (t, J = 123.9 Hz, $NC=C(O)\underline{C}H_2$), 34.2 (d, J = 125.1 Hz, $CH_2)_2\underline{C}H$), 31.7 (q, J = 125.5 Hz, $C(\underline{C}H_3)_3$), 31.4 (d, J = 125.7 Hz, $\underline{C}H(CH_3)_2$), 20.82 (q, J = 126.8 Hz, $CH(\underline{C}H_3)_2$), 20.8 (q, J = 126.8 Hz, $CH(\underline{C}H_3)_2$), 11.6 (q, J = 126.2, $C_5(\underline{C}H_3)_5$). IR (cm^{-1}, KBr, cast): 2959 (m), 2905 (m), 2864 (m), 2820 (m), 1646 (m, C=C), 1440 (m), 1380 (m), 1362 (m), 1358 (s), 1301 (s), 1277 (vs), 1253 (m), 1220 (vs), 1081 (vs), 1050 (m), 1020 (m). MS Calcd for $C_{32}H_{51}ONTi$ *m/e* 513.34501, found 513.33990.

Titanocene Amidoenolate 196b from Iminoacyl Complex 191b:



Isopropyl bis(pentamethylcyclopentadienyl)titanacyclobutane(cyclohexyl amido)enolate 196b. In the drybox, a Fischer-Porter bottle was charged with a toluene solution (10 mL) of iminoacyl complex **191b** (189 mg, 0.37 mmol) and assembled. The sealed vessel was taken out of the drybox and the solution cooled to -78°C for 0.5 h. The vessel was then pressurized with CO (60 psig) and the reaction mixture allowed to warm slowly to room temperature over a period of 10 h. The excess CO was vented from the reaction vessel and it was then taken into the drybox where the toluene solution was removed *in vacuo*. The residue was dissolved in 0.5 mL of pentane and cooled to -35°C to yield dark brown needles (170 mg, 85%). Spectroscopic and high resolution mass spectrometry data for complex **196a**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 2.77 (m, 1H, C$\underline{H}$(cy)), 2.40 (m, 2H, C$\underline{H}_2$), 2.28 (m, 2H, C$\underline{H}_2$), 1.85 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.84 (s, 15H, $C_5(C\underline{H}_3)_5$), 1.79 (m, 5H, C$\underline{H}_2$(cy)) 1.53 (m, 1H, $CH_2)_2C\underline{H}$), 1.27 (m, 5H, C$\underline{H}_2$(cy), C$\underline{H}(CH_3)_2$), 0.94 (d, J = 6.6 Hz, 6H, $CH(C\underline{H}_3)_2$). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 143.8 (s, C=$\underline{C}$-O), 122.9 (s, $\underline{C}_5(CH_3)_5$), 122.8 (s, $\underline{C}_5(CH_3)_5$), 110.3 (s, N-$\underline{C}$=C), 41.0 (t, J = 128.4 Hz, $\underline{C}H_2)_2CH$), 40.8 (d, J = 126.4 Hz, N-$\underline{C}$H(cy)), 36.7 (t, J = 128.0 Hz, $\underline{C}H_2)_2CH$), 34.0 (d, J = 125.6 Hz, $CH_2)_2\underline{C}H$), 32.1 (d, J = 123.5 Hz, $\underline{C}H(CH_3)_2$), 27.4 (t, J = 125.5 Hz, $\underline{C}H_2$(cy)), 27.3 (t , J = 125.5 Hz, $\underline{C}H_2$(cy)), 26.2 (t, J = 126.6 Hz, $\underline{C}H_2$(cy)), 20.9 (q, J = 124.7 Hz, $CH(\underline{C}H_3)_2$), 20.7 (q, J = 124.7 Hz, $CH(\underline{C}H_3)_2$), 11.9 (q, J = 126.5 Hz, $C_5(\underline{C}H_3)_5$), 11.8 (q, J = 126.4 Hz, $C_5(\underline{C}H_3)_5$). IR (cm^{-1}, KBr, cast): 2954 (s), 2923 (s), 2909 (s), 2864 (s), 2852 (s), 2819 (m), 1628 (m, C=C), 1540 (s), 1447 (s), 1374 (s), 1363 (m), 1324 (vs), 1316 (vs), 1233 (s), 1198 (m), 1138 (s), 1018 (s). MS Calcd for $C_{35}H_{53}ONTi$ *m/e* 539.36066, found 539.35875.

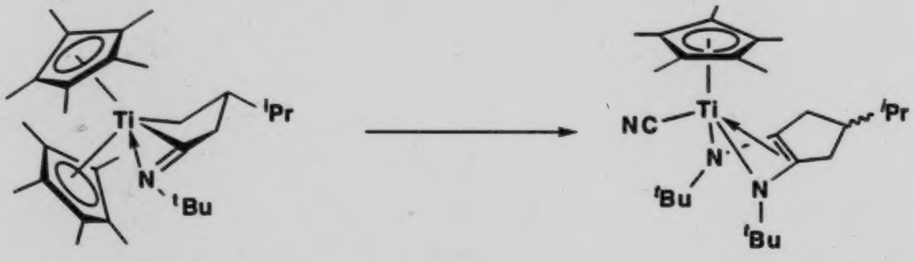
Half-Sandwich Titanocene Enediamidate 197 from Titanacyclobutane 47g:



47g **197**

Cp*(CN)Ti[bis(*tert*-butyl)enediamidate 197. In a 25 mL Schlenk flask, isopropyl bis(pentamethylcyclopentadienyl)titanacyclobutane **47g** (74.0 mg, 0.184 mmol) in pentane was cooled to -78°C. *tert*-Butylisonitrile (34 µL, 3 equivalents) was added to the cooled solution and after 30 minutes at this temperature, the reaction mixture was allowed to warm to room temperature and stirred for 2.5 h. Removal of the solvent yielded a dark green solid, which was crystallized from cold hexane (-35 °C) to yield dark green cubes (66.0 mg, 78%). See below for spectroscopic and analytical data for complex **197**.

Half-Sandwich Titanocene Enediamidate 197 from Iminoacyl Complex 191a:



191a **197**

Cp*(CN)Ti[bis(*tert*-butyl)enediamidate 197. In a 25 mL Schlenk flask, complex **191a** (11.0 mg, 0.233 mmol) in toluene was cooled to -78 °C. Excess *tert*-butylisonitrile (10 µL, 3 equivalents) was added to the cooled solution and after 30 minutes at this temperature, the reaction mixture was allowed to warm to room temperature and stirred for 2.5 h. Removal of the solvent yielded a dark green solid, which was crystallized from cold hexane (-35 °C) to yield dark green cubes (11 mg, quant.). ^{1}H NMR analysis indicates the presence of two isomers in a 1:1 ratio in which the Cp* ligand and the isopropyl substituent are either *syn* or *anti* to each other. X-ray quality crystals of the *syn* isomer were obtained from a cold hexane solution (-35 °C). Spectroscopic and analytical data for complex **197**: ***syn* isomer**: ^{1}H NMR (400.1 MHz, C_6D_6): δ 2.88 (dd, *J* = 14.6, 8.1 Hz, 4H, $C\underline{H}_2)_2CH$), 2.10 (m, 1H, $CH_2)_2C\underline{H}$), 1.91 (s, $C(C\underline{H}_3)_3$), 1.89 (s, $C_5(C\underline{H}_3)_5$), 1.49 (m, $C\underline{H}(CH_3)_2$),), 0.91 (d, *J* = 3.2 Hz, 1H, $CH(C\underline{H}_3)_2$). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 156.1 (s, $\underline{C}N$), 121.0 (s, $\underline{C}_5(CH_3)_5$), 110.5 (s, $-\underline{C}=\underline{C}-$), 59.9 (s, $\underline{C}(CH_3)_3$), 44.9 (d, *J* = 126.2 Hz, $CH_2)_2\underline{C}H$), 35.3 (t, *J* = 133.8 Hz, $\underline{C}H_2)_2CH$), 34.1 (d, $\underline{C}H(CH_3)_2$), 32.1 (q, $C(\underline{C}H_3)_3$), 21.4 (q, *J* = 125.4 Hz, $CH(\underline{C}H_3)_2$), 12.9 (q, *J* = 126.9 Hz, $C_5(\underline{C}H_3)_5$). IR (cm^{-1}, KBr, cast): 2962 (m), 2926 (m), 2905 (m), 2077 (w, CN), 1460 (m), 1358 (m), 1284 (m), 1203 (m), 1023 (m), 795 (m), 510 (vs). ***anti* isomer**: ^{1}H NMR (C_6D_6, 400.1 MHz): δ 2.62 (dd, *J* = 14.2, 4.8 Hz, 4H, $C\underline{H}_2)_2CH$), 2.22 (m, 1H, $CH_2)_2C\underline{H}$), 1.51 (m, $C\underline{H}(CH_3)_2$), 1.29 (s, $C_5(C\underline{H}_3)_5$), 1.26 (s, $C(C\underline{H}_3)_3$), 0.89 (d, J = 3.1 Hz, 1H, $CH(C\underline{H}_3)_2$)). ^{13}C NMR (100.6 MHz, C_6D_6, gated decoupled): δ 156.1 (s, $\underline{C}N$)), 121.0 (s, $\underline{C}_5(CH_3)_5$), 110.3 (s, $-\underline{C}=\underline{C}-$), 60.0 (s, $\underline{C}(CH_3)_3$), 42.3 (d, J = 135.0 Hz, $CH_2)_2\underline{C}H$), 34.1 (d, $\underline{C}H(CH_3)_2$), 33.6 (t, J = 133.8 Hz, $\underline{C}H_2)_2CH$), 31.9 (q, $C(\underline{C}H_3)_3$), 19.8 (q, J = 124.0 Hz, $CH(\underline{C}H_3)_2$), 12.6 (q, J = 126.4 Hz, $C_5(\underline{C}H_3)_5$). Anal Calcd (as a mixture) for $C_{27}H_{45}N_3Ti$: C, 70.18; H, 10.09; N, 9.03. Found C, 70.57; H, 9.87; N, 9.14. Selected X-ray crystallographic data for complex **197** are listed at the end of experimental section (p. 267).

SELECTED CRYSTALLOGRAPHIC DATA FOR COMPLEXES 151 AND 197

Selected X-Ray Crystallographic data for Bis(2-piperidinoindenyl)titanium cinnamyl 151.

Additional information (including structure factors, etc.) can be obtain directly from Dr. Robert McDonald at the University of Alberta Molecular Structure Center, Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2 Canada. Request report # *jms9710.rep*.

Table 4.1. Crystallographic Experimental Details of Cinnamyl Complex **151**

A. *Crystal Data*	
formula	$C_{37}H_{41}N_2Ti$
formula weight	561.62
crystal dimensions (mm)	0.38 × 0.36 × 0.34
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters[a]	
a (Å)	16.688 (2)
b (Å)	15.369 (2)
c (Å)	12.160 (2)
β (deg)	109.285 (10)
V (Å^3)	2943.7 (7)
Z	4
ρ_{calcd} (g cm^{-3})	1.267
μ (mm^{-1})	0.319
B. *Data Collection and Refinement Conditions*	
diffractometer	Siemens P4/RA[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–60
scan type	θ–2θ
data collection 2θ limit (deg)	50.0
total data collected	5461 ($-19 \le h \le 18, 0 \le k \le 18, 0 \le l \le 14$)

Table 4.1. Crystallographic Experimental Details (continued)

independent reflections	5192
number of observations (*NO*)	2418 ($F_o^2 \geq 2\sigma(F_o^2)$)
structure solution method	direct methods/fragment search (*DIRDIF–96*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9186–0.8800
data/restraints/parameters	5191 [$F_o^2 \geq -3\sigma(F_o^2)$]/0/361
goodness-of-fit (*S*)[e]	1.052 [$F_o^2 \geq -3\sigma(F_o^2)$]
final *R* indices[f]	
$F_o^2 > 2\sigma(F_o^2)$	**$R_1 = 0.0868$**, $wR_2 = 0.1382$
all data	$R_1 = 0.2046$, **$wR_2 = 0.1832$**
largest difference peak and hole	0.311 and –0.331 e Å^{-3}

[a] Obtained from least-squares refinement of 49 reflections with $21.0° < 2\theta < 26.0°$.

[b] Programs for diffractometer operation and data collection were those of the XSCANS system supplied by Siemens.

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[d] Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections except for 1 having $F_o^2 < -3\sigma(F_o^2)$. Weighted *R*-factors wR_2 and all goodnesses of fit *S* are based on F_o^2; conventional *R*-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. *R*-factors based on F_o^2 are statistically about twice as large as those based on F_o, and *R*-factors based on ALL data will be even larger.

[e] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0495P)^2]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 4.2. Selected Interatomic Distances (Å) of Cinnamyl Complex **151**

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ti	C1	2.318(6)	C10	C18	1.427(8)
Ti	C2	2.351(6)	C11	C12	1.439(8)
Ti	C3	2.448(6)	C12	C13	1.424(8)
Ti	C10	2.442(6)	C12	C17	1.418(8)
Ti	C11	2.454(6)	C13	C14	1.343(9)
Ti	C17	2.407(6)	C14	C15	1.397(9)
Ti	C18	2.331(6)	C15	C16	1.374(8)
Ti	C30	2.462(6)	C16	C17	1.429(8)
Ti	C31	2.409(6)	C17	C18	1.435(8)
Ti	C32	2.480(6)	C19	C20	1.534(8)
Ti	C37	2.456(6)	C20	C21	1.506(9)
Ti	C38	2.386(6)	C21	C22	1.530(9)
N1	C10	1.416(7)	C22	C23	1.510(9)
N1	C19	1.453(7)	C30	C31	1.417(8)
N1	C23	1.463(7)	C30	C38	1.418(8)
N2	C30	1.409(7)	C31	C32	1.423(8)
N2	C39	1.462(7)	C32	C33	1.401(8)
N2	C43	1.469(7)	C32	C37	1.432(8)
C1	C2	1.387(8)	C33	C34	1.378(9)
C2	C3	1.381(8)	C34	C35	1.383(10)
C3	C4	1.480(8)	C35	C36	1.361(10)
C4	C5	1.396(9)	C36	C37	1.419(8)
C4	C9	1.392(8)	C37	C38	1.433(8)
C5	C6	1.378(8)	C39	C40	1.509(8)
C6	C7	1.382(9)	C40	C41	1.527(8)
C7	C8	1.376(9)	C41	C42	1.501(9)
C8	C9	1.365(9)	C42	C43	1.524(8)
C10	C11	1.401(8)			

Table 4.3. Selected Interatomic Angles (deg) of Cinnamyl Complex **151**

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C1	Ti	C2	34.6(2)	C10	Ti	C38	140.7(2)
C1	Ti	C3	62.1(2)	C11	Ti	C17	56.5(2)
C1	Ti	C10	135.6(2)	C11	Ti	C18	57.0(2)
C1	Ti	C11	102.6(2)	C11	Ti	C30	131.4(2)
C1	Ti	C17	99.8(2)	C11	Ti	C31	120.4(2)
C1	Ti	C18	135.0(2)	C11	Ti	C32	134.7(2)
C1	Ti	C30	112.9(2)	C11	Ti	C37	165.0(2)
C1	Ti	C31	136.9(2)	C11	Ti	C38	159.4(2)
C1	Ti	C32	114.1(2)	C17	Ti	C18	35.2(2)
C1	Ti	C37	82.9(2)	C17	Ti	C30	139.8(2)
C1	Ti	C38	81.5(2)	C17	Ti	C31	106.0(2)
C2	Ti	C3	33.4(2)	C17	Ti	C32	90.6(2)
C2	Ti	C10	111.0(2)	C17	Ti	C37	109.1(2)
C2	Ti	C11	79.5(2)	C17	Ti	C38	143.4(2)
C2	Ti	C17	107.6(2)	C18	Ti	C30	109.2(2)
C2	Ti	C18	133.2(2)	C18	Ti	C31	77.6(2)
C2	Ti	C30	112.6(2)	C18	Ti	C32	78.0(2)
C2	Ti	C31	146.4(2)	C18	Ti	C37	109.3(2)
C2	Ti	C32	144.7(2)	C18	Ti	C38	132.6(2)
C2	Ti	C37	111.0(2)	C30	Ti	C31	33.8(2)
C2	Ti	C38	94.2(2)	C30	Ti	C32	55.6(2)
C3	Ti	C10	103.6(2)	C30	Ti	C37	55.7(2)
C3	Ti	C11	83.4(2)	C30	Ti	C38	34.0(2)
C3	Ti	C17	132.4(2)	C31	Ti	C32	33.8(2)
C3	Ti	C18	137.8(2)	C31	Ti	C37	56.4(2)
C3	Ti	C30	85.0(2)	C31	Ti	C38	57.2(2)
C3	Ti	C31	116.8(2)	C32	Ti	C37	33.7(2)
C3	Ti	C32	136.8(2)	C32	Ti	C38	56.9(2)
C3	Ti	C37	111.4(2)	C37	Ti	C38	34.4(2)
C3	Ti	C38	80.8(2)	C10	N1	C19	113.9(5)
C10	Ti	C11	33.3(2)	C10	N1	C23	115.2(5)
C10	Ti	C17	57.0(2)	C19	N1	C23	114.8(5)
C10	Ti	C18	34.7(2)	C30	N2	C39	112.7(5)
C10	Ti	C30	106.8(2)	C30	N2	C43	112.4(5)
C10	Ti	C31	87.6(2)	C39	N2	C43	111.9(5)
C10	Ti	C32	104.3(2)	Ti	C1	C2	74.0(4)
C10	Ti	C37	138.0(2)	Ti	C2	C1	71.4(4)

Selected X-Ray Crystallographic data for Cp*(CN)Ti[bis(*tert*-butyl)enediamidate 197.

Additional information (including structure factors, etc.) can be obtain directly from Dr. Robert McDonald at the University of Alberta Molecular Structure Center, Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2 Canada. Request report # *jms9608.rep*.

Table 4.4. Crystallographic Experimental Details of Complex **197**

A. *Crystal Data*	
formula	$C_{27}H_{45}N_3Ti$
formula weight	459.56
crystal dimensions (mm)	0.48 × 0.41 × 0.14
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters[a]	
a (Å)	16.4949 (4)
b (Å)	9.4610 (3)
c (Å)	17.5737 (9)
β (deg)	94.381 (3)
V (Å^3)	2734.5 (2)
Z	4
ρ_{calcd} (g cm^{-3})	1.116
μ (mm^{-1})	2.761
B. *Data Collection and Refinement Conditions*	
diffractometer	Siemens P4/RA[b]
radiation (λ [Å])	Cu Kα (1.54178)

Table 4.4. Crystallographic Experimental Details of Complex **197** (continued)

monochromator	incident-beam, graphite crystal
temperature (°C)	–60
scan type	θ–2θ
data collection 2θ limit (deg)	113.5
total data collected	3780 ($0 \le h \le 17$, $0 \le k \le 10$, $-19 \le l \le 19$)
independent reflections	3633
number of observations (*NO*)	3292 ($F_o^2 \ge 2\sigma(F_o^2)$)
structure solution method	direct methods (*SHELXS–86*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*[d])
absorption correction method	empirical (face-indexed)
range of transmission factors	0.6900–0.3544
data/restraints/parameters	3630 [$F_o^2 \ge -3\sigma(F_o^2)$]/0/280
goodness-of-fit (*S*)[e]	1.033 [$F_o^2 \ge -3\sigma(F_o^2)$]
final *R* indices[f]	
$F_o^2 > 2\sigma(F_o^2)$	$R_1 = 0.0524$, $wR_2 = 0.1374$
all data	$R_1 = 0.0574$, $wR_2 = 0.1454$
largest difference peak and hole	0.497 and –0.402 e Å^{-3}

[a] Obtained from least-squares refinement of 36 reflections with $58.2° < 2\theta < 58.9°$.

[b] Programs for diffractometer operation and data collection were those of the XSCANS system supplied by Siemens.

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on F_o^2; conventional R-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. R-factors based on F_o^2 are statistically about twice as large as those based on F_o, and R-factors based on ALL data will be even larger.

[e] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0727P)^2 + 3.6590P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 4.5. Selected Interatomic Distances (Å) of Complex **197**

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ti	N2	1.915(2)	C5	C7	1.414(6)
Ti	N3	1.922(3)	C7	C8	1.493(6)
Ti	C1	2.177(4)	C7	C9	1.472(6)
Ti	C2	2.361(3)	C10	C11	1.490(5)
Ti	C3	2.361(3)	C10	C12	1.529(6)
Ti	C30	2.408(3)	C10	C13	1.488(6)
Ti	C31	2.378(3)	C20	C21	1.520(5)
Ti	C32	2.353(3)	C20	C22	1.526(5)
Ti	C33	2.397(3)	C20	C23	1.536(5)
Ti	C34	2.410(3)	C30	C31	1.394(5)
N1	C1	1.141(4)	C30	C34	1.417(5)
N2	C2	1.384(4)	C30	C35	1.499(6)
N2	C10	1.482(4)	C31	C32	1.415(5)
N3	C3	1.381(4)	C31	C36	1.508(5)
N3	C20	1.479(4)	C32	C33	1.410(5)
C2	C3	1.389(4)	C32	C37	1.499(5)
C2	C6	1.508(4)	C33	C34	1.396(5)
C3	C4	1.513(4)	C33	C38	1.507(5)
C4	C5	1.539(5)	C34	C39	1.503(5)
C5	C6	1.493(5)			

Table 4.6. Selected Interatomic Angles (deg) of Complex **197**

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
N2	Ti	N3	91.43(11)	C3	Ti	C33	109.36(12)
N2	Ti	C1	94.42(12)	C3	Ti	C34	142.72(13)
N2	Ti	C2	35.89(10)	C30	Ti	C31	33.87(12)
N2	Ti	C3	67.09(10)	C30	Ti	C32	57.05(12)
N2	Ti	C30	111.98(12)	C30	Ti	C33	56.59(13)
N2	Ti	C31	98.92(11)	C30	Ti	C34	34.22(13)
N2	Ti	C32	118.24(12)	C31	Ti	C32	34.81(12)
N2	Ti	C33	152.65(11)	C31	Ti	C33	57.09(12)
N2	Ti	C34	145.61(12)	C31	Ti	C34	56.71(12)
N3	Ti	C1	98.39(12)	C32	Ti	C33	34.52(13)
N3	Ti	C2	67.09(11)	C32	Ti	C34	56.94(12)
N3	Ti	C3	35.81(11)	C33	Ti	C34	33.76(13)
N3	Ti	C30	155.92(12)	Ti	N2	C2	89.9(2)
N3	Ti	C31	140.45(12)	Ti	N2	C10	145.8(2)
N3	Ti	C32	107.60(12)	C2	N2	C10	124.2(3)
N3	Ti	C33	99.91(12)	Ti	N3	C3	89.7(2)
N3	Ti	C34	122.92(12)	Ti	N3	C20	146.5(2)
C1	Ti	C2	122.45(11)	C3	N3	C20	123.5(3)
C1	Ti	C3	124.29(11)	Ti	C1	N1	177.3(3)
C1	Ti	C30	85.79(12)	Ti	C2	N2	54.22(14)
C1	Ti	C31	118.50(13)	Ti	C2	C3	72.9(2)
C1	Ti	C32	136.76(13)	Ti	C2	C6	142.2(2)
C1	Ti	C33	108.25(13)	N2	C2	C3	119.2(3)
C1	Ti	C34	80.00(12)	N2	C2	C6	129.6(3)
C2	Ti	C3	34.23(10)	C3	C2	C6	110.1(3)
C2	Ti	C30	129.94(12)	Ti	C3	N3	54.51(15)
C2	Ti	C31	100.74(11)	Ti	C3	C2	72.9(2)
C2	Ti	C32	99.61(11)	Ti	C3	C4	143.7(2)
C2	Ti	C33	128.66(12)	N3	C3	C2	119.6(3)
C2	Ti	C34	155.64(11)	N3	C3	C4	129.5(3)
C3	Ti	C30	149.79(11)	C2	C3	C4	110.1(3)
C3	Ti	C31	116.16(11)	C3	C4	C5	104.5(3)
C3	Ti	C32	95.65(11)	C4	C5	C6	106.5(3)

Table 4.6. Selected Interatomic Angles (continued)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C4	C5	C7	121.6(4)	Ti	C31	C30	74.2(2)
C6	C5	C7	123.4(4)	Ti	C31	C32	71.6(2)
C2	C6	C5	105.8(3)	Ti	C31	C36	123.7(3)
C5	C7	C8	116.3(4)	C30	C31	C32	108.1(3)
C5	C7	C9	119.6(4)	C30	C31	C36	126.1(4)
C8	C7	C9	113.7(4)	C32	C31	C36	125.7(4)
N2	C10	C11	108.8(3)	Ti	C32	C31	73.6(2)
N2	C10	C12	105.4(3)	Ti	C32	C33	74.4(2)
N2	C10	C13	114.9(3)	Ti	C32	C37	125.2(3)
C11	C10	C12	107.8(4)	C31	C32	C33	107.7(3)
C11	C10	C13	110.1(4)	C31	C32	C37	125.4(4)
C12	C10	C13	109.6(5)	C33	C32	C37	126.2(4)
N3	C20	C21	107.1(3)	Ti	C33	C32	71.0(2)
N3	C20	C22	107.7(3)	Ti	C33	C34	73.6(2)
N3	C20	C23	112.9(3)	Ti	C33	C38	126.2(3)
C21	C20	C22	109.4(3)	C32	C33	C34	108.1(3)
C21	C20	C23	109.2(3)	C32	C33	C38	126.0(4)
C22	C20	C23	110.4(3)	C34	C33	C38	125.6(4)
Ti	C30	C31	71.9(2)	Ti	C34	C33	72.6(2)
Ti	C30	C34	73.0(2)	Ti	C34	C30	72.8(2)
Ti	C30	C35	123.8(3)	C30	C34	C33	108.1(3)
C31	C30	C34	108.0(3)	Ti	C34	C39	125.5(2)
C31	C30	C35	126.6(4)	C30	C34	C39	125.9(4)
C34	C30	C35	125.3(4)	C33	C34	C39	125.7(4)

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